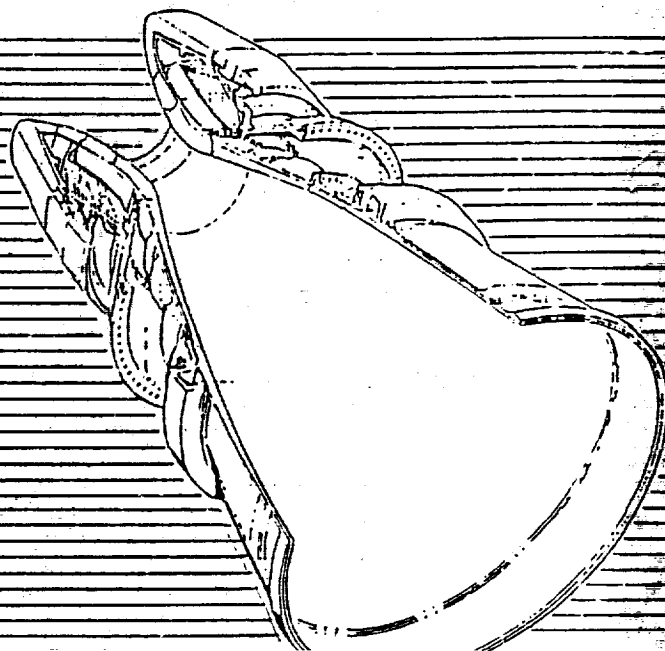


MINUTES
ADVISORY COMMITTEE
ON STANDARDIZATION OF CARBON - PHENOLIC TEST
METHODS AND SPECIFICATIONS
SANTA ANA, CA

MAY 16, 1989



Mississippi State
University

MINUTES OF THE ADVISORY COMMITTEE
ON STANDARDIZATION OF CARBON - PHENOLIC TEST
METHODS AND SPECIFICATIONS FOR
STANDARDIZATION OF THE CARBON-PHENOLIC AND
CARBON-CARBON MATERIALS AND PROCESSES

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MINUTES
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ON STANDARDIZATION OF C-P TEST
METHODS AND SPECIFICATIONS SANTA ANA, CA
MAY 16, 1989

for
Standardization of the Carbon-Phenolic and
Carbon-Carbon Materials and Processes
NASA Grant No. NAG8-545

Prepared for
National Aeronautics and Space Administration
George C. Marshall Space Flight Center, Alabama 35812

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October, 1989

AGENDA
SPIP - Nozzles

Advisory Committee on Standardization
of Carbon-Phenolic Test Methods and Specifications

U. S. Polymeric
Division of Hitco
Santa Ana, CA
May 16, 1989

9:00 - 9:10	Welcome by John C. H. Chang President, Hitco Materials Division
9:10 - 9:20	Introduction, Bill Hall Mississippi State University Committee Chair
9:20 - 9:30	Overview of SPIP Status Jay Larson, Hercules
9:30 - 10:30	Carbon Fibers Oxidation Testing Round Robin Results -R. Yost, Fiberite -T. Day, MTL/W -M. Towne, Amoco -P. Pinoli, LPARL
10:30 - 12:00	North American Rayon 2nd Source Program -Dr. Turbak -D. Beckley on D-5 Effort, USP -L. A. Fikes on NASA Effort, MSFC
12:00 - 1:00	Lunch
1:00 - 2:00	GPC Resin Advancement Testing -T. Bhe, ASPC -F. Bancroft, USP
2:00 - 3:00	Carbon Assay Testing -G. Rubin, Hitco -T. Paral, Polycarbon -M. Towne, Amoco
3:15 - 3:30	Ultrasonic Testing for Resin Content -D. Beckley, USP
3:30 - 3:45	Review of JANNAF/SPIP meeting on CCP testing MSFC 34 May -B. Hall, Mississippi State University -L. A. Fikes, NASA/MSFC
3:45 - 4:00	General Remarks of Test Methods Eric Stokes, SoRI
4:00	Open Discussion and Committee Recommendations

ATTENDEES AT
ADVISORY COMMITTEE ON
STANDARDIZATION OF CARBON - PHENOLIC TEST
METHODS AND SPECIFICATIONS
SANTA ANA, CA
MAY 16, 1989

NAME	ORGANIZATION
Pat C. Pinoli	Lockheed Research
William B. Hall	Mississippi State University
Tom Bhe	Aerojet Techsystems
Thomas A Paral	Polycarson, Inc.
Myles K. Towne	Amoco Performance Products, Inc.
Gene Rubin	Hitco
Eric Stokes	Southern Research Institute
Kevin Clemons	Aerojet Solids
Tom Sreenivasan	Aerojet Solid Propulsion
Dick Herman	Hercules, Inc.
Gloria A. Whitaker-Daniels	Lockheed Missles and Space
John Stites, Jr.	U. S. Polymeric
Jim Thomas	ICI Fiberite
Clarke B. Lium	U. S. Polymeric
Ed Hemmelman	ICI Fiberite
Suzanne Beimer	ICI Fiberite
Rob Yost	ICI Fiberite
Lou Ann Fikes	NASA MSFC
Stephen Tan	Kaiser Aerotech
Al Turbak	Consultant
Karl-Heinz Schofalvi	Kaiser Aerotech
Don Beckley	U. S. Polymeric
Joan K. West	Mississippi State University
Edward Mills	CSD

- D. Beckley My host, Tom Spooner, who is vice-president and general manager of the facility here, would like to say a few words before we begin today's agenda. Tom.
- T. Spooner Thanks, Don. You will be happy to hear that my remarks will be brief. I just want to welcome all of you to U. S. Polymeric and to tell you that I believe that this is a worthwhile endeavor that you are all working on materials specifications, test procedures, and so on toward better materials control. All of you know that this work has been long overdue in some areas, and we certainly appreciate the effort that everyone is putting out. I want to welcome all of you from the many companies participating, Marshall Space Flight Center, and some of our competitors, so I hope you enjoy your day at U. S. Polymeric. I understand that you are going on a tour later and will have an opportunity to see at least one vertical treater here and some of our laboratory facilities. Enjoy yourselves. You are in good hands with Don Beckley, John Spikes, and Clark Williams, and I hope that you enjoy your stay. Have a fine day. Thank you.
- D. Beckley Bill, do you want to say anything?
- B. Hall No, I think we have covered the location of the facilities, so let's go ahead.
- B. Hall My name is Bill Hall. I am from Mississippi State University and am part of the SPIP program out of Marshall. Specifically, this committee is concerned with the constituents of the rocket nozzle that is up to the prepreg, before fabrication Program. 3.2.1 is concerned with the constituents (the phenolic resin, carbon cloth, filler, and prepreg) and the test methods, specifications, and test equipment used to qualify these materials. Our job is to look at the test methods and procedures under two guidelines: (1) does the test method that we use accurately measure the property that we are trying to measure and (2) if this property is measured correctly, does it give us any useful information. Both of these criteria must be met before we are satisfied, and if not, then we should concern ourselves with the test methods and specifications.
- I assume that all of you are familiar with the material flow, the materials for the prepregger. We will start with the prepregger. We have two--U. S. Polymeric and Fiberite. They both use three materials in prepregging--carbon cloth, a filler, and a phenolic resin. As we take the cloth back to the beginning, we have Avtex in Fort Royal, VA that makes the rayon. Lou Ann will talk to us this morning about the efforts to have a second source for our rayon precursor. Weaving is done by one company, Highlands, at Cheraw, SC. The woven rayon then is shipped to one of three carbonizers, Polycarbon, Amoco and Hitco; they all carbonize, then supply the two prepreggers in various amounts. The

two resins, one which is furnished by Borden, and the other is furnished by Ironsides. They both use their own proprietary fillers, which are now very similar in properties. Are there any questions about the flow sheets.

For some of you this is your first meeting and for your information, the entire proceedings are taped, transcribed, and typed. Then each of you are sent a copy of the minutes in order that you can correct your part of the minutes and return it us. Then we print the final product; therefore, we need copies of all handouts that you use--all view graphs, charts, or anything that you use--so that they can be placed in the proceedings. Are there any questions before we get started? Joan West will be handling all the paperwork and the typing, and she will be calling you if there are any questions about your part on the program. She will pass circulate the sign-up sheet. Normally, we get your name, address, and telephone number, but this time we would also like to have you put your fax number under your phone number because sometimes it is more convenient to fax.

As I indicated earlier, we are a part of the SPIP program. The general contractor for SPIP is Hercules, and Dick Herman of Hercules is going to bring us up to date where we are on the SPIP program at this time.

D. Herman

Bill asked me to do a general summary of the status of SPIP nozzles. It strikes me as I look around the room that anyone in here could probably do a better job of summarizing where the SPIP nozzle program is than I can. I am filling Jay Larson's shoes today since he is tied up in a proposal, commonly known as NRA Initiatives. I think all of you know what is going on there. The end of the month is the time limit for the proposal.

The SPIP program, as envisioned by people such as Marion Kitchens, NASA headquarters, had within it seven initiatives. The objective of the program is solid propulsion reliability and has been established to improve the success rate of U. S. solid rocket motors by improving the basic engineering understanding and capabilities of the system. The seven initiatives were initially established included nozzle and bond lines. As we all know, both have been funded and Hercules is involved in both of them. The composite case and the joint seal programs have not been, and probably, will not be funded. They both received wide attention from Morton-Thiokol earlier. Programs funded within Marshall are the propellants, combustion dynamics, and verification. To implement the SPIP nozzle program, we looked at three major areas that we commonly refer to as how to design it better, build it better, and inspect it better. These major areas are further delineated as Task 3.1--Materials Characteristic, Design Analysis, and

Capabilities--How to design it better using a better knowledge of consistent materials and models; Task 3.2--Calls for better understanding of the manufacturing process and the process variability; and Task 3.3--Product Evaluation and Verification--How to inspect and test what you built. You want to see if you have built it the way you wanted to build it through NDE, instrumentation, and the use of simulating test beds. We organized the team with Lockheed and Dr. Frank Weller of Palo Alto, heading Task 3.1--Materials Characterization Effort. Companies working with him include Boeing, FAA, PDA Engineering, Atlantic Research, Kaiser, Acurex, and Southern Research. Task 3.2, is run by Ed Higgs at Hercules. Ed will be retiring at the end of this month and will be replaced by Jay Larson. Helping Jay run initiative 3.2 include Lockheed, Boeing, Atlantic Research, Southern Research, Hitco, Fiberite, U. S. Polymeric, PDA, Southern, SAIC, and FAA. Task 3.3--Product Evaluation Verification is being run by John Schrader of Boeing, and he is being helped by Lockheed (Lockheed Aerospace Systems), FAA, and PDA.

When I accepted this job, I was told that probably my biggest challenge was to try to keep these 15 or 20 very capable and sometimes very independent team members from all going the same direction. That has not been a problem. If anybody deserves credit for the results of this program, it has to go to all members of our team and to all of you in this room. I can't thank you enough. Both Hercules and I express our appreciation to each of you for helping make this program work.

I will give you a little more detail on Task 3.2.1.1, although I'm sure that many of you know as much about it as I do. Task 3.2.1.1--Constitute and Prepreg Testing and Test Methods Assessment--is being headed by Pat Pinoli at Lockheed, Palo Alto. The objective of the program is to assess current methods and identify any needed improvements. The method by which those needed improvements and methods will be evaluated will include, among other things, round-robin testing. The status today is, as Pat has identified, five tasks involving four constituent tests. The test methods defined, as of today, are in many cases considered to be inadequate. There may even be some cases where there are some testing procedures that are unsafe, and one of the examples cited is the DMF method and a question about carcinogens. The next task is monitoring a second source of rayon activities, and we will hear more about that.

To cover the investigations, Pat has completed a schedule. Detailed discussion of the five task forces is the subject of this meeting today. With completion of the work that has been identified by Pat in 1989, we are expecting to do additional tests and investigations in 1990.

Task 3.2.1.2--Carbon-Carbon Exit Cone Technology is being headed by Liz Emery of Hercules. The objective of the task is to identify three carbon-carbon exit cone technologies that have the greatest potential for development. The method of evaluation will be by completion of questionnaires by 11 fabricators. Many of you in this room have completed these questionnaires. The answers will be summarized, and a scoring system will be developed which will be used to score the various procedures and processes that are used by fabricators. The results and recommendations resulting from that study will be submitted to NASA In July, 1989.

- P. Pinoli At our last committee meeting, there was a strong emphasis on CVD densification and Hercules made an initial recommendation for a CVD densification process. You guys were to come out with recommendations for total PPG.
- D. Beckley The intent of this program, though, was to lay out a facility down at Marshall and the idea was to make a recommendation as to what kind of facility Marshall should put in place to allow them to develop the activity for the future. I was somewhat concerned that the emphasis seemed to be coming out of this quarterly with the strong recommendation for total densification capability.
- D. Herman We are driven by many things, including the availability of funding at Marshall Space Flight Center. There is a mid-term review scheduled during the week of June 19 at Marshall to see what the facility will look like and to get some feedback as to whether or not this is the facility that is perceived to be affordable. The preliminary design has both LOPIC and CUD densification capabilities.
- P. Pinoli My concern is that most exit cone manufacturing companies use primarily CVD in thin shell structures and NASA needs this capability. Thick c/c components, however, use liquid pitch or thermoset resin densification which require additional equipment.
- D. Herman I believe that I am certainly hearing what you are saying, and the question would be "Is there, in the scope, something beyond thin-shell exit cones under consideration?" If you are talking thick hardware, the general understanding is that we do not get CVD as deep as we want it in thick walled structures; therefore, the facility, if it is going to be usable, needs to be able to go several ways.
- P. Pinoli That is not easy to do without greatly expounding the proposed facility equipment needed. I agree that CVD densification must be recommended, but it would be a mistake to limit the capabilities that NASA should have.
- P. Pinoli Well, is there any coordination to what you are doing?

L. Fikes I do not know.

P. Pinoli Is NASA totally ignoring the issue c/c parts to be densified i.e., exit cones, ITE, etc.?

L. Fikes I do not know. You will have to ask somebody else.

P. Pinoli I was just curious.

D. Herman It is not something that has totally been ignored.

P. Pinoli The Edwards Astronautics lab expressed a similar need for a c/c facility; they got it and now they need industry support to operate it.

D. Herman The status of the 3.2.1.2 program as of this week is that we have received answers back to our questionnaires from 11 of the 13 fabricators; the summary of their answers has been completed, and this week Liz Emery will be Fedexing packages to the people who are going to do the scoring; there are some in this room who will receive those packages this week. We are going to be pressing very hard to answer all the questions and inviting you to a meeting at the end of the month. The date has not been designated when we will all sit together and review the total results and make sure that everyone understands the questions, the answers, and what the final recommendations will be. That report, in rough draft form, will be due out in June, with the final report due in July.

Task 3.2.1.3--PAN Selection--is being headed by Charlie Heyborne. The objective of that program is to identify the PAN based material systems. A system for applications to the exit cones and thrusts are being considered separately. The selection method is to down select, based on literature search, to twelve candidate materials for both throats and exit cones. Those candidate materials will be fired in three 2-inch throat nozzles at MSFC. FM-5-55 will be in each firing to be used as base-line data. The status of that program today is that 4 throat candidates and 6 high density and 2 low density exit cones candidates have been selected. Six materials are at Kaiser, being fabricated. Those materials will be delivered to American Automated for inclusion in the nozzle. The design of the nozzle is complete, including the instrumentation. American Automated is on schedule with the manufacturer of metal parts of the nozzle; Nasa is preparing for the first of 3 tests in July, 1989, provided that we can support that test schedule by delivering the first nozzle. The last firing will be in October of 1989. At the end of these firings, we will down select to the 3 candidates and go on to the next level of selection using the Hercules Brutus motor.

- T. Bhe Are those the mechanical properties used in the down select data. Are those the high temperature data?
- D. Herman Those high temperature data are the part of the initial selection of the first prepreg materials.
- T. Bhe In the last 3.1 meeting, it was brought out that there is no standard procedure for performing the mechanical properties test. east test laboratory uses different test geometry, method of heating up the sample in testing the tensile property of the composite.
- D. Herman Yes, there are data. We hope to improve that. Finally, Aerojet Solid Propulsion Company is on board today in the name of Scott Brown. They are preparing to support us with cure cycle work beginning immediately after the first of the 3 nozzle tests. All of this should come about in the third quarter of 1990.
- D. Beckley Dick, I would like to comment at this point. I cannot say this with a large degree of finality, but I recall in many of the small motor testings that preceeded all of the work that basically fills our understanding of materials performance, when we were in small motors, 2 inches and under, there was much misleading data generated because we heat sinked the nozzle itself in the test area directly to the steel case. Essentially, that became a water cooled structure. What happened was that we ended up with materials that had very high conductivities, and that is, in essence, where we are headed. A number of these looked excessively good and did not even generate an unacceptable charring because the conduction was so great. It was not until we insulated the throats, significantly, or until we got into the 9-inch motor, where there is no longer any insulation provide to us, that the true performance of the materials showed up. Now, my observation of the 2-inch nozzle, unfortunately, indicates that this looks like a repeat of that other history. I hope I am wrong, but I am concerned that as an evaluator of what is going to happen, we may be setting ourselves up to make a selection that will not really work out in the long run.
- T. Bhe If someone wants a reference, we can return to citing some firings that once were done at Sacramento. Basically there was a standard material test holder which was either a paper phenolic or silica phenolic (approximately a 2-inch thick insulator); the test insert dropped into that can. That was the mechanism used in a 3/4 inch throat to essentially isolate the material from the test beds.
- D. Herman Don, your concern is valid. At this point we are doing comparison testing, using FM-5055 as a base.
- D. Beckley Okay.

D. Herman The rationale for this suggests that this will be an good test; we have 6 or 8 materials in 1 nozzle throat.

D. Beckley But the material with the largest sink will run the coldest and, essentially, will look the best. Later on you do not have that sink available to you and things have a habit of turning around. That is all I am concerned about. We need to be able to read through the results or at least factor in this sink issue.

J. Thomas Is Brutus the 2-inch throat you are talking about?

D. Herman No.

J. Thomas What size is it?

D. Herman We will be able to go to an approximate 7 to 7 1/2 inch throat. We will fill it up, about 20,000 pounds of propellant.

D. Beckley It is kind of analogous to the JPL, only taller.

D. Herman Yes.

D. Beckley I do not believe the comment applies to Brutus as it does to that 2-inch motor.

D. Herman Brutus has been used about 6 times. Are there any other questions or comments?

B. Hall Thank you very much, Dick. As Dick indicated, Pat Pinoli is the principal investigator from Lockheed on the particular section of the SPIP that we are dealing with. Pat will introduce the 4 areas that we are talking about today, plus the second source.

P. Pinoli Before we get started, I want everyone to recognize that we do operate this meeting in an open forum setting. Please feel comfortable; do not feel that we have too much decorum here. If you want to get up and get a cup of coffee, please do so. The idea is to exchange data, have a good time, feel free to say what you want to say. You can always correct your taped input later.

A. Turbak The keeper of the tapes says "No you will not."

P. Pinoli We want to allow everyone to address the technical issues up front. Do not worry about it too much. If you have a question, please ask it directly and do not wait until later when you forget about it and put it off. This is an interactive type meeting; feel free to move around and feel comfortable.

 I want to introduce you to the activity on the oxidation rate testing. For those of you who have not been to a

previous meeting, I will give you some background as to why we are doing this particular testing and what we are looking for. Task 1 revolves around a test procedure that was introduced into the shuttle program about 2 years ago (as an engineering test). The intent of the test was to measure the oxidation rate of carbon fabric to ensure that carbon fabric which supported combustion did not get into the program. We had some material very early (approximately 5 years ago) that got into the program that behaved something like this (Fig.1). This is 525°C some isothermal oxidation rate data. You can see the weight change of material being heated up to 525°C. In this case we programmed 3 minutes, up the temperature. The initial weight loss is rather high, going up to 525°C. The rationale for that is the loss is adsorb moisture. At 550°C, a linear oxidation rate was exhibited with a rapid decrease as the surface area increased. After essentially 30 minutes of temperature, the matter was totally gasified. The engineering test incorporated into the procedure was to monitor the carbon fabrics that were coming into the program to ensure that this type of material did not get into ablative nozzle parts. Typical CCA3, CSA and VCL, with a moderate to low sodium level will provide fairly good oxidation resistance. WCA is fired much higher and provides excellent oxidation resistance. I might throw in another caveat. We did a large amount of experimental work on this fabric which shows that in a solid rocket nozzle exhaust environment, this material is not that sensitive to mass loss because the exit gas coming out of the nozzle is primarily reducing in nature. We found that the cut off point, with respect to the sodium level, is something like 1600 parts per million. Unless you exceed 1600 parts per million, you could not measure a difference in mass loss weight with respect to the sodium level.

Next I will present results of some round-robin testing which we initiated about 6 weeks ago. In order to get this program running, I wrote the standard procedure for the Perkin-Elmer equipment. We used Perkallloy as the calibration metal samples of fabric in to short lengths, about 1 mm long and used glass vials to protect the sample from environmental exposure. Lou Ann, do you have a sample vial that we might show people? We sent out the series of 9 samples each to 4 laboratories--Morton-Thiokol, Fiberite, Lockheed, and Amoco. We tried to reduce variability of samples sent to each laboratory by cutting a large batch of each carbon fabric in to 1 mm long filaments, mixing the batch, and, finally, introducing each batch of chopped fiber into glass vials. We then considered the boats that we used for the TGA. At Lockheed we had seen some effect from the platinum boats (conventional for measuring PGA), and we felt that there was a catalytic action by platinum with the carbon specimen. So we went to a quartz boat (the standard material that is used in conjunction with academic carbon

testing). We sent out quartz boats to everyone who was a part of this test program and tried to ensure that the amount of material being tested was within some bounds (4 mg was a reasonable amount of packing into the small boat). We required that everyone fall within the guidelines that were indicated and provided a small device to prepack all the filaments into the boat. Essentially, we took a very small glass tube, placed the filaments into it, packed them down into a preform, then preform was transferred into the boat. This provided a specimen consistency with respect to aspect ratio and how the fibers are packed into the boat. Then we had to make sure that everyone used the same type of clean air in the test apparatus, and we extended the heating time to heat up the sample from 3 to 5 minutes. We extended the heating time from room temperature to 525°C from 3 minutes to 5 minutes to provide better rate control and prevent temperature over run. We felt that there was a possibility of getting some overshoot. The formal test procedure that all the laboratories followed is enclosed in the appendix. The test is designed to measure the total mass loss after 30 minutes at 525°C. In addition to this data, however, the TGA plot provides the mass loss associated with heat up from room temperature to 525°C. This loss factor is primarily residual volatile (water) in the carbon fabric sample.

- D. Beckley At this point, I will turn the program over to Rob Yost from ICI, Tempe, Arizona. Rob will talk about round-robin results. Just as an understanding--are you starting your zero point after that 5-minute induction time? Is that zero weight?
- P. Pinoli Yes. The data that we are using for interpretation is strictly the 5-to 35-minute time zone.
- K. Schofalvi I am not sure that what these data represent are not taking the initial 5-minute loss at the zero starting point.
- R. Yost We took the 9 samples that Pat prepared and ran them through the 525°C test (Fig. 1). We performed 2 runs after our instrument was brought into calibration. We have no data for CCA-3 lot 42063 because we used the sample up on previous testing. We are seeing a much higher weight loss for the CSA North Hollywood material than for the other samples, and the run-to-run reproducibility of the testing is less than ideal. Previously we had done 10 repeat runs on each of the 10 samples and found a relative standard deviation of 5 to 8 percent. This data was run before we had calibrated the instrument properly.
- P. Pinoli Rob, would you review what each of the 9 fabrics represent? I failed to do that initially.
- R. Yost At this point Pat, I believe that you have actually answered the question as to which samples were which.

- G. Rubin Is there any reason why your run 2 is always higher than your run 1?
- R. Yost We performed the run 1 tests on all the samples and then went back and performed the run 2 tests. There may be some day-to-day variation in the instrument that caused the run 2 to be higher.
- D. Beckley [No, recognized reason...]
- R. Yost This TGA that we have is very sensitive to furnace height. The temperature the pan sees is not necessarily the same as the recording thermocouple. If the length of the hangdown wire changes after the instrument is calibrated, the calibration is no longer valid even though the thermocouple output to the computer has not changed. We performed the 525⁰C isothermal tests the first time and compared our results with Pat Pinoli and found our weight losses were double his. We tracked down the source of the differences as improper calibration (wrong furnace height), corrected the furnace height, and reran the samples giving the data shown in Figure 1.
- P. Pinoli This is new data, then, as opposed to the initial 10 runs.
- R. Yost Yes, this is new data. The old data was generated using a calibration procedure which uses Perkalloy and alumel as cure point standards to calibrate the temperature response in the software. The hardware itself is not really calibrated in this procedure, only compensated for. To get around the problem, we decalibrated the software and ran the Perkalloy at different furnace heights and determined where the hardware was in calibration. At this point the software was calibrated using the two standards, and the results of the calibration and testing were much better.
- P. Pinoli Rob, did you talk to my people with respect to furnace height?
- R. Yost The Perkin-Elmer service engineer recommended that we vary the furnace height and monitor the results. It looks like the furnace height will be a critical parameter in this type of testing. Pat also asked me to perform the isothermal weight loss test at 457⁰C. His thoughts were that the rate of oxidation would be different at the lower temperature and might be a better discriminator of poor stability fiber. The weight losses were much lower at 475⁰C than at 525⁰C as expected, and, again, the North Hollywood material was much less stable than the other samples; the WCA was much more stable, and the others were in the same neighborhood as each other (Fig. 2). Again, the same pattern was observed: run 1 was lower than run 2.

- D. Beckley What about your furnace height that you corrected?
- R. Yost All of this data was run after the furnace height was adjusted to the proper height. We had run 90 tests before we discovered how critical the height was, and it was very painful not to be able to use that data. We performed another experiment to answer the question of how the temperature of the isothermal hold affects the weight loss. The hold temperature was varied from 450°C to 540°C in 10 C increments on CCA-3 lot 42352 and the data is shown in Figure 3. The curve is smooth with no knee point(s) and is headed up in an exponential manner.
- P. Pinoli You need to point out that these mass loss values were generated over a temperature range.
- R. Yost We were complaining very loudly about the fact that the TGA, when decalibrated, was reading 530°C for the cure point of Perkalloy when it should have been 596°C. The software calibration was having to correct the temperature response curve by 60°C to bring it into calibration, and I thought that was ridiculous. I wanted the hardware to be much closer to the actual temperature before the software had to correct the curve so that the Perkin-Elmer service people said to adjust the furnace height. We then ran an experiment adjusting the furnace height using Perkalloy to determine the proper furnace height.
- P. Pinoli The data that I have seen at 475°C suggest that we still have a problem with respect to lab-to-lab variability. The variability at 475°C is less, but so is the mass loss values; therefore, the co-efficient of variance remains about the same. Your "activation energy" run data was interesting to us and we found our data plots out on semi-log paper very similar to yours. The slight off set suggests a small calibration difference.
- D. Beckley Do you think that varies from day to day?
- R. Yost Probably not. That is why I think we see some day-to-day variation. If the balance hangdown wire gets little kinks in it, it may change the height of the sample in the furnace which will change the temperature the sample is at. It may be changing all over the place, causing test temperature variations in an unpredictable manner. We did not seem to have any problems with static or fugitive fibers. Our weight loss curves were very smooth (no jumps in the curve) which indicates that no fibers were jumping out of the sample pan, and the furnace was not hanging up on the side of the furnace. In that respect we seem to have a good test procedure.
- P. Pinoli Some of our TGA curves exhibited extensive chatter.

- R. Yost We have an 800 pound bench top that the TGA sits on which is very stable and helps minimize the chatter in the curves.
- P. Pinoli We are working with very small samples, 4mg, and we were concerned at Morton-Thiokol that the fibers were blowing out of the boat itself. That should give periodic, very sharp drops in the TGA plot. Unfortunately, what we were seeing in our data was a lot of up and down chatter which indicated to me that the fibers may be jumping up and down. It is interesting because it gave me the feeling that there may be some other forces involved; it could be that desorption gasses were coming out or air flow pulses were developing.
- R. Yost If we see any chatter in our data at all, it is at the very beginning of the test during heat up. We normally see a small rise in the weight possibly due to convective currents inside the furnace due to driving the temperature up to 100°C minimum.
- P. Pinoli Rob, the bottom line, though, is do you feel more comfortable with the new procedure providing meaningful data?
- R. Yost Yes. I think that we have success in a test that tells us if we have horrible fiber or more acceptable fiber. I do not know whether it would be appropriate to set specifications on the fabric at this point.
- P. Pinoli What would you recommend that we do next to follow up on this?
- R. Yost I think we need to track fiber through a test firing and try to correlate the TGA test data and any other testing with the performance of the finished material. If the TGA test is significant then the ablation rates of material should be related to the TGA weight loss. At this point, we do not have enough data to decide if it is.
- P. Pinoli As long as the test can discriminate a North Hollywood fabric, then I can be satisfied.
- R. Yost The only thing that you can do is decide which of the test temperatures is the one that you feel comfortable with.
- D. Beckley I was reviewing the parametric study done on North Hollywood process and its sensitivity of showing the same thing in the TGA, but I don't know if you remember the data. Essentially there is an increase in through-put of a significant amount which caused the TGA to do just that--it just fell away into the low weight retention thing (a drop of number degrees centigrade). Did you do a -100 or -200?

- R. Yost What do you mean? Do you mean through the parametric study?
- D. Beckley My point is that I think the data for the first time (the TGA data of the experiments) shows the data for the TGA in explaining or showing up a material that would otherwise have passed the existing spec altogether. In other words, we had a good carbon assay, but it did not have the thermal stability of the standard typical material. So, to help processors and convertors not inadvertently to get into that area, I do think that the TGA has value at this point.
- J. Thomas Don, was that not a use of a high sodium content, though?
- D. Beckley No. This was the parametric study, Jim, where sodium content was not really an issue. If you run your process faster or you run your process at a lower temperature, both of them produced a high sodium content instead of a weight retention of what we are seeing here (either 2% or 15 % weight loss); they produced fibers like the North Hollywood material that basically had the 0 to 20% retention. There will be a marked difference if you get the process way out of kilter. I had never seen any other test data that showed that as graphically as this TGA data.
- J. Thomas I do not remember hearing him explain that.
- D. Beckley I have the material with me today where his earlier explanation came from so that we can look at during break if anyone would like to.
- P. Pinoli Jim, to add to your comment--I think we have a three-fold consideration: the amount of surface area present, the accessibility of that surface area to oxygen, and sodium concentration.
- J. Thomas Are you addressing crenulation, Pat, when you say "surface area"?
- P. Pinoli No. That is a minor contribution to surface area, but crenulation lobe voids create higher permeability.
- J. Thomas That is not a bag of worms that I think we need even visit. (group discussion)
- P. Pinoli Okay, Miles, it is now your turn to discuss Amoco data.
- D. Herman Pat, refresh my memory for a minute. I cannot remember what this North Hollywood stuff is. I think I have heard you say that. What is its significance?
- P. Pinoli The significance of North Hollywood material is that it is involved in both STS-8A and 17B. The two worst cases of pocket erosion were connected with this material.

Management at NASA was quite impressed with some of the TGA when they saw that this material had such a poor oxidation resistance. That was one thing they zeroed in on and it scared them. All of the other parameters we talked about--low carbon assay, high surface area, and moisture adsorption capacity--are treated as a puzzle. No one understood how they interacted with the performance of the material. The material will disappear at a very low temperature in air; that is frightening.

- J. Thomas When you talk about testing, I think you will find that when you take the same material and put it into a different environment, you will not get the same results because the same material tested at Morton-Thiokol will not yield the same results as if it were tested at Marshall. It can be misleading because of the difference in sample size.
- P. Pinoli By using the current MTI specification procedure, we have shown that the results cannot be duplicated.
- J. Thomas Not only the development of the North Hollywood material with a sodium content but also at least high surface area were the sole cause. I just do not want to go out and indict a material merely on that basis because of the many manufacturer problems that would go along with that.
- P. Pinoli I think that it is important to note, Jim, that the 2 worst cases of pocket erosion were with North Hollywood fabric. That is all I am saying. I do not think there is anyone here who feels comfortable with using a material with such a poor oxidation resistance; we want something better, and I know we can get it. The only thing we are looking for is a discriminator test that ensures that you do not allow poor oxidation resistant fabric to enter the shuttle program.
- J. Thomas I think that TGA is probably moving in that direction, but I do not think we need to adopt TGA testing just yet as the savior for the problems of high sodium and oxidation rate. I think there is some understanding to go along with that.
- M. Towne That is a good introduction. I think TGA will probably identify North Hollywood material. I have several problems when you try to assign it a number and use it as an acceptance test between labs. I will begin today with some excerpts of a recent talk presented by one of the Amoco people at GE entitled An Accelerated Oxidation Test for Oxidation Resistant Carbon Fibers. TGA was one of the studies done, and the conclusion is that the TGA does not distinguish the way you want to distinguish; there are problems with it that I will discuss later on in the program.
- We use the DuPont not the Perkielmer because we have the DuPont. One of the things that we found when we were trying to get started with this is that we were having trouble with

the equipment--getting the temperature up. After several false starts with the equipment people, we decided that we would just heat up the furnace, insert a sample into it, and then we would get a rapid rise in temperature (we did very well in 2 to 2 1/2 minutes). We inserted the sample into the temperature and got this temperature rise (Fig.). One of the things, the low fire examples, lost a lot of moisture during heat up in the first 2 to 3 minutes of the test. We had to alter the procedure. We also wanted to address some other things, and I did not want to use Pat's samples for this. I did not like the idea of chopping up the samples and packing them in because, to me, it introduces an unnecessary variable. We studied, some years ago, a 1983 vintage VCL that happened to have this much sodium in it, and we did the test at 25 cc per minute to 525⁰ C. We cut a standard diameter disc, the weight of which is about 3 grams rather than your 3/10 of a gram, out of the fabric with a cork borer. (several talking at once)

D. Beckley Approximately what size cork borer did you use, Miles?

M. Towne It is an 8mm.

D. Beckley 3 mg.

M. Towne Yes. (group discussion) No, 16 mg. Our unit has a standard platinum pan. Earlier today Pat discussed the concern of our oxidation of carbon with the catalyzation of that oxidation reaction with platinum. None of our people at Parma believed this. We did it (Fig. 2) at the standard 25cc per minute, and we did duplicate runs--putting that disc in a platinum pan. These are duplicate runs, I think, done on different days. We also felt that in oxidation test (spelled out in Bernard's report), when you are up in this range, oxidation is so fast on some of these that you get limited diffusion. You are not measuring the rate of oxidation, but you are measuring the availability of oxygen to complete the reaction. So we went to 100cc per minute, and we got more oxidation, again very reproducible results.

We thought we would take a look at aluminum to see if that made any difference. We used aluminum pans and we got a little more than we did on the platinum (Fig. 2) I am not sure why we got a little bit more.

Then we went to Pat's little boat, the little crucible. The sketch on the board is a quartz ring that is about 6 mm in diameter, a loop. We took Pat's little crucible, set it in there, and we did the test. We cut up the filaments, so this was similar to what Pat sent us. We ran the same 25cc and we got 38.6% weight loss on this (Fig. 2). As you can see, there is certainly not much difference from platinum. We feel that this really does not tell us if there is a catalyzed reaction going on.

We were concerned about how that crucible would affect the availability of air around the sample while it was being oxidized, we took the disc and laid it across the top of the loop so that now there was no confinement and it had a ready supply of air. You have a reproducible sample, and we did quite a few of the tests that way. If you will look (Fig. 2) we did get what we expected, a little bit higher, though, where it was a bit more confined.

D. Beckley Is there any evidence that....

M. Towne No.

D. Beckley That was my only concern.

M. Towne I think when you do it in the disc, Pat, these things stay together pretty good if you handle them....

J. Thomas Are you worrying that sodium is maybe not a big driver?

M. Towne I do not think that the difference between 150 ppm and 1000 would be very significant. Now, here is the comparison of the results (Fig. 3), and this is Pat's crucible. These are all the numbers that we can compare now with raw data, but it is with a different piece of equipment. There is some variability here that if I thought these were the same materials, I would say we were handling them differently. Packing them is one way that we are handling them differently. I was concerned about that. These two are the same; the North Hollywood is gone in 10 minutes. The VCX 13 was lowered minutely; maybe we had .10 of a percent or whatever with the WCA. In comparison with an 8mm disc fabric disc, that we set on top of this loop, we felt that we had more control of the samples. The polycarbon, CSA materials, all come in very close. One CCA material is a little different (Fig. 3). This one showed up higher in all other series of testing that I have seen. So, I think there is a difference between this one, CCA-3 42099 and these two.

We also looked at the 475⁰ C, thinking that at least in that there might not be a difference in the 475. We did not do all of them, but we did one. These numbers are higher than what Rob showed. Again, in his curve, if we plot our numbers here, we are lying at a higher level.

D. Beckley In other words, you had an offset.

M. Towne Yes, we had an offset. Again, this is a very good distinguisher here (Fig. 4), and a difference here. We wanted to take a look at chlorate at 475 with a 25cc per minute at a 100 on this one sample after the initial loss. We had 5.2

percent loss in 30 minutes at the 25cc and 6.2 and there is still a difference.

- D. Beckley Miles, the first number compared to the original number in Figure 4 are repeats.
- M. Towne This is a a repeat of this. We took out the initial loss, which I think is a problem and how to handle that moisture.
- P. Pinoli Is this single point data?
- M. Towne These are all single point. We were rushing at the end, Pat, after we got things rolling. I want to hit on a couple of other things first. One, you probably have seen this from something I did several years ago, and this is something that you were talking about. Figure 5 shows a range of oxidation. This is circulating air hanging in an oven and this is the type of test that is proposed finally, in this paper that I distributed earlier.
- P. Pinoli Was this Bernard's?
- M. Towne Yes. I did this, which I think is the same one except that we are missing the 1090 ppm₉ (Fig.1). I think that that is the same VCL. Figure 5 denotes 3 differences ; I do not think that we are talking about too much here. This was the STS-8 type material that was shooting off, very easily distinguished in a test in the 24-hour range. The test that is recommended in this paper is the 16 hour test that can be run overnight. The way that that test is run is in oxygen because we are talking about more oxidation resistant fibers. They did 72 samples at a time, so from a production standpoint, it is a very easy test to do.
- D. Beckley Have you had a chance to run multiple or different amounts of samples in the same oven? In other words, if you load an oven up with 70 samples or you run 3 samples, do you get different numbers? Our experience on other testing would indicate that that might be expected.
- M. Towne We have plenty of air coming into this. In case of the oxygen, one that they recommend, Don; they actually were concerned about fiber flight and we had to put up screens in the system. But the oxygen flow rate is indicated to be very high.
- D. Beckley This is a larger sample, right.
- M. Towne Yes, this is a piece of fabric that is about 2 to 3 inches square, and this is the material that we now call VCX 12, which is just fired at approximately 200⁰ higher. WCA in this test still shows you nothing. I think that this is the kind of test that could be appropriate on these materials. Now, the one that discusses in his paper will be

available when we get this out. By the way, this test is one that was developed for the General Electric high temperature fiber application. Celanese, Hercules, and Amoco have all been involved with this at GE and have done some round robin type testing to see how applicable that is.

- D. Beckley So, the curve was off the 375, and they settled on 430 and are testing pan materials?
- M. Towne Yes, in oxygen for 16 hours.
- D. Beckley Not enhanced oxygen, just air?
- M. Towne No. Oxygen.
- D. Beckley Pure, circulating oxygen?
- M. Towne Yes.
- D. Beckley Now you have a test cost of oxygen.
- M. Towne It was needed for the oxidation of the fibers to find out where pans fit. There was a big difference between that....
- D. Beckley Was your other curve, the VCL curve, in air?
- M. Towne Yes. I think that for the kind of materials that we are talking about here, air is very adequate.
- J. Thomas Miles, did you say you were doing one sample per test?
- M. Towne When it is done in the oven--I think they are doing 3 samples each time--this will show you (Fig. 6) a lot of materials. There are 2 levels in the rack and there is obviously a difference of about 1 percent here, but that is pretty small compared to the data in Figure 5.
- J. Thomas Normally, you did one sample per test?
- M. Towne When I did those....
- J. Thomas Would not that change the test results and give us more material than you have indicated here?
- M. Towne In the test that I showed earlier, the VCL in air, those were triplicate samples and I had 5 or 6 different samples.
- J. Thomas I know, but you said 3, and that is what
- M. Towne Yes, the oven had more than that. We always included the sample of the same material from run to run for comparison. We had to make sure that the temperature was the same because if there is a couple of degrees difference in an extended test, it would cause different results.

- D. Beckley This is not 1 material, but 2 positions top and bottom and 10 or so in each one in a range of 7 to 11, so is either number just as good?
- M. Towne Yes, we are talking about 6 to 9.
- G. Rubin How were you protecting the samples from fiber loss?
- M. Towne They wind off a couple of layers to make sure that there is no possibility of contamination; then the layers are wound in little piece of equipment that makes it so that there is about 3 grams and these. The layers are handled with gloves; they are put into the oven and dried, first, to make sure that the starting point is the same. These are quickly weighed and replaced in the oven and the oven height goes up and down. This technique is discussed in Bernard's paper.
- D. Beckley But that is only appropriate for fiber?
- M. Towne Yes. Actually fabrics are much easier because you can just hang the fabric on a hook.
- D. Beckley But getting a difference between 7 and 11 would kind of bother me as, you know, if the acceptance level were 9.
- J. Thomas Don, I agree. That is a pretty good spread.
- M. Towne I will have to take a look at the paper again. There may be difference in the fibers. I know that that is the case in this one and you get a difference here between 105 and 100, but those are different there.
- P. Pinoli How does he treat the sizing. Is it unsized material or does he burn it off?
- M. Towne He burns it off in the drying. It only takes a few minutes.
- E. Hemmelen What temperature is that?
- P. Pinoli I think he uses 470°C. We have seen excellent results of 470°C burn off, indicating that 5 minutes at that temperature is more than adequate to remove all the sizing on the carbon fiber.
- M. Towne That is in the paper. Now, back to the TGAs on the DuPont and what we considered reproducibility. These are 2 of the CSA samples that tell you what we were able to do (Figs. 7 & 8) with our temperature and the method that we were using. (placing two overheads on top of each other) This is our temperature curve for 3 minutes and once we were able to get this thing going, we were able to hit that temperature again, right on the button. These are 2 of the different

samples, CSA 0539 and 0567. The DuPont furnace is pretty hot when samples are introduced, but we thought that the reproducibility is pretty good.

Pat talked about the buoyancy effect and the crucible. Looking at the VCX material, which has very little moisture on it, you get this jump. When you have (several talking at once about Fig. 9). This is one of the CSAS where you have moisture and have washed out the buoyancy effect and you are immediately into this weight loss; on one of these others here, I think I show that effect more dramatically. We took the derivative curve to see what was happening; this was VCL which, of course, had some moisture, and we were able to pick up the buoyancy effect. But this is the rate of weight loss, which, as you can see, occurs by the time we are up to 350°C. This is one of our earlier runs using the Pt pan technique.

- D. Beckley If you had predried the specimen, you would have predicted the buoyancy effect to be greater?
- M. Towne It would look like the VCX. WCA was the same. I think that is my story. Pat, I think that the reproducibility between labs is going to vary because anything we did differently created a significant difference in the results. We heated everything exactly, but the results changed whenever we changed the procedure.
- P. Pinoli We have definite indication of high lab-to-lab variance.
- D. Beckley Miles, is it a recommendation of yours to consider the larger sized hanging specimen in air circulating oven as an in lieu?
- M. Towne I think the largest size specimen in the air circulating oven is a better test. I think that if you are going TGA, I would recommend something like this where you do not do anything to the sample except cut a uniform sample so that it is not interfered with
- D. Beckley We still may have expected that the TGAs would have offsets.
- M. Towne But, I think that it might minimize them, just looking at the 3 CSA materials when they are different when they are packed in the crucible.
- T. Bhe What would be your explanation for these differences?
- M. Towne I think then that your packing is going to be different and your availability of air around the sample would be a variable.
- P. Pinoli I have to admit that I like Miles' sample procedure since all of my previous work has been on 2 x 2 inch squares. Do you

remember that, Gene. We put them into aluminum dishes, into a dead air oven and measured weight loss. We found that it was an excellent discriminator between fabric specimens, and we could easily track the firing temperature of the carbon fabrics. We never looked at the complete picture as to whether we were tracking firing temperature alone or sodium level and/or surface area. The firing temperature influences all of these aspects. I never felt that the oxidation test had to discriminate exactly why the behavior was different. It simply was to identify that there was a behavior difference. I might also comment that all this data is fresh. I have not seen Miles' data beforehand, and it presents several surprises. This is the first time that I have had a chance to see it, and we are going to have to digest it.

To give you some feel for LPARL data, I'll try to go through this quickly. We made 3 series of runs at Palo Alto. The first series gave us single run data. We got this sequence, which is relatively low, from the other data presented (Fig. 2). Subsequently we decided to make another series of runs. Triplicate runs made in over a period of two days developed pretty good data with respect to standard deviation. But, here again, if we compare our data with everyone else's, we are offset. The general trends, however, are always present. We get the North Hollywood material which is very high in oxidation rate; I do not think that I have seen the same trend that Miles was seeing with regard to the CCA3 having a slightly higher oxidation rate. Instead if anything I am seeing that our offset is slightly higher.

- G. Rubin Among the three, the same one is .
- P. Pinoli I am always intrigued with fact that the VCX 13, just by going a little higher in temperature, dramatically effects the oxidation rate mass loss values.
- J. Thomas Pat, based on that data there, North Hollywood, if you just had that laid in front of you, would you say that all the others were acceptable for use?
- P. Pinoli Oh, surely. I would say that these 3 samples are comparable to these (Fig. 3).
- J. Thomas Where would you start rejecting? What range are you talking about?
- P. Pinoli The reject rate may be at this level here (Fig. 4). This is the material we are concerned about.
- J. Thomas Is 50 or 60 unacceptable?
- P. Pinoli That has to be established and must be related to the isothermal temperature we use.

- D. Beckley Jim, you have to is being used come back and say whose piece of equipment at that point. 50 or 60 on one might be the same as 20 on another.
- P. Pinoli Before I continued this 525⁰C test work, we reduced the temperature. I think that the 475 data is better. This is the third series of tests that we ran, and since we have only single run data, we do not have standard deviation (Fig 5). If we show the same standard deviation data that showed up in the ICI tests, then this is a reasonable discriminator. We can definitely say that North Hollywood fabric is significantly different than the 3-CCA3 and 3 CSA fabrics. VCX 13 intrigues me because it is not significantly different.
- E. Hemmelman Yes, but it is, than what I got. almost double.
- J. Thomas That is a higher....
- P. Pinoli It is fired about 100 to 200⁰C higher.
- M. Towne It should have been similar, Jim, to the view graph that I had with the 3 higher sodium and the one down near the WCA.
- P. Pinoli I am not going through all of this data because we are running behind schedule, but this is the first run plot, what I call the residual volume level for the samples (Fig.6). Frankly, I made no attempts, when we prepared these samples, to control the environment of the samples prior to packaging them into these glass vials. They were cut in the ambient lab conditions, packed into the vials, and sent out. Apparently in doing so the North Hollywood material had an ability to pick up more water. This 7.69 percent represents at least 90 percent water. The other fabrics picked up less than 3 percent water.
- D. Beckley Is this the same that had the same high weight loss also. It makes it suspect. It just does not behave.
- P. Pinoli The initial 5 minutes of heating WCA actually gained weight. As the sample is heated, the air in the furnace is lighter and provides a slight increase in specimen weight.
- E. Hemmelman Is that buoyancy effect less than all these materials?
- P. Pinoli It is interesting that you should bring that up. This is a typical TGA curve that we get and the buoyancy effect that we are talking about here (Fig. 7). You have to keep in mind that that buoyancy effect is being off set by the loss of water in the sample. In our last meeting in Utah, I was intrigued with the fact that North Hollywood fabric did not reflect a strong buoyancy effect. What this suggests to me is that the moisture in this material is not only higher, but it is also having greater difficulty diffusing out. It has to

do with the microporosity and the nature of the activated carbon structure. Possibly one of the problems that we are dealing with with this type of fabric is not only does it have the tendency to trap or adsorb more moisture, but that moisture is also retained for a longer period of time during the firing condition. When it is released, it has reached a higher temperature and possibly exhibiting a higher pore

- J. Thomas This is North Hollywood material in lot 1100 that went into material.
- P. Pinoli This is part of roll 10B of the polycarbon parametric study.
- T. Paral This was not made at .
- P. Pinoli It was designed by Polycarbon.
- J. Thomas (Inaudible)
- P. Pinoli In passing, I want to make 2 comments with regard to side studies that have been performed. One of them was to look at the issue of flow rates and impingement of the air on the sample itself. The P/E apparatus has a small jet stream that brings air directly into the sample. The flow rate of air is controlled. We investigated the effect of higher air flow rate on the sample and found very little effect on mass loss rate.
- He also looked at the fiber aspect ratio. We were concerned that if we prepacked the sample to make a preform, then filaments are broken up and the aspect ratio changes. We made 2 runs in which he really worked the material very heavily and broke up the filaments. Essentially, the results indicated very little difference--29 vs 30 percent weight loss.
- D. Beckley The occlusion that is availability of surface air to the sample, Miles, open disc vs packed sample seems to produce different numbers.
- P. Pinoli I continue to feel that we are working at a very sensitive 525°C. When the temperature is reduced, I think that we are going to reduce some variable effects. It is hard, at this point from the data that I've seen, to discriminate run-to-run effects that we are interested in looking at. I think that if one sample is run today and another is run tomorrow, there is enough variability to mask some of the effects. I believe that the platinum catalyzation effect is probably one of those things being masked out in the Amoco data.
- A. Turbak There is a lot of data here. Has anyone plotted this to try to determine if it is over temperature?
- P. Pinoli The activation energy analysis, yes.

- A. Turbak From that you should be able to discover whether you have a different mechanism cracking at 525, and also you should be able to know whether you have catalyses problems.
- P. Pinoli I am sure it is going to work out that way, and work is under way to use that approach.
- A. Turbak Has it come up yet?
- P. Pinoli It will work out.
- A. Turbak I am sure you have picked it up, but it will give you the exact point where your mechanism changes.
- D. Beckley The temperature curve is a kind of parabolic third order. It does not seem to have a break.
- A. Turbak If you were to plot that a different way, though, you may get a crack in your $1/t$ -curve vs weight loss. At that point you have a different mechanism coming in to the weight loss.
- P. Pinoli I appreciate that. I think that that is the way to investigate the fundamentals.
- A. Turbak It is entirely coming in if you get 2 kinetic rates. It is important for you to know that.
- P. Pinoli The activation energy of the carbon oxygen reaction is well known. You are right.
- A. Turbak But whether it is going into formaldehyde or to CO_2 or CO will tell you immediately from your activation energy.
- P. Pinoli If I can find my plot that parallels what Rob did, , I'll get off the podium. Basically I attempted to duplicate what Rob did, and if you look at both plots, you will see that they look about the same. What we have to do is look at the activation energy of each data set and compare pre-exponential factors.
- A. Turbak You have a problem because you must have catalysis coming in. That would tell you that either residues in your fibers or something else is causing the catalysis, which is critical. You have not picked it up. I think that this will help you. It looks to me like you have too much (inaudible) around 5 .
- P. Pinoli Yes., I will be doing some work on that.
- A. Turbak It is critical for you, if you are going to exceed that temperature, that you get a far more rapid degradation.

- P. Pinoli I guess that it is my feeling that you should stay below that critical temperature and increase the time so that you can have a better differentiation.
- A. Turbak If you are sure that you are not going above that temperature, then....
- P. Pinoli Then you are not missing critical data.
- A. Turbak In natural performance, then, you are kidding yourself. The other thing that should come out of that is that if you do not come out with 21 kcal per mole, then you know that you are in catalysis. If you come down lower than that in your curve, then you know you have a catalytic effect of some kind.
- D. Beckley Miles, in the old carbon and graphite handbook of Union Carbide, there is an activation chart for various fibers. It is like an Appendix to the carbon and graphite monolithic materials, and it shows activation temperatures for WCA, VCK, and so forth.
- M. Towne I will have to go back and look at that.
- J. Thomas Pat, I have a question. SPS9B-218A (Inaudible), starting with 218A (Inaudible) have you seen anything of this type that shows sensitivity to that material?
- P. Pinoli No.
- J. Thomas I think you are down into the (Inaudible)
- D. Beckley The performance difference there should have been something other than the material because there was no material change during that period and the pocketing disappeared. We can credit the fabricator with making improvements.
- J. Thomas The point that I want to make is that if 8A had not occurred, then the pocketing that occurred on 9B would have been a significant enough occurrence to be . There is no reason to determine that.
- D. Beckley I do not think the test by itself would solve any one particular problem, but it is contrived to try to keep us out of a catastrophic problem.
- J. Thomas It certainly would distinguish between North Hollywood material.
- D. Beckley Yes. No one wants to put that kind of material into a motor.
- P. Pinoli My only concern about this interpretation is that a lot of what people perceive as pocket erosion, to me, reflects wedge out (the two components coming together and having

short piles). People would look at that and not say it is pocket erosion. I think that the mechanism for failure is different. I am talking about material that is lost within the confines of the part itself. The thing about 17B that intrigued me is that the regions that pocketed were distinctly North Hollywood material. The material right above it, CCA3, looked great.

We need to take about a 12-minute break.

B. Hall

Dr. Turbak, a consultant to Morton-Thiokol and NASA on this particular effort, will now speak to us.

A. Turbak

I thought I would build up some background. If it is inappropriate, because I did not know what the group wanted at the first meeting, then stop me. I would like to open with a disclaimer; since I have signed a non-disclosure agreement with North American Rayon, I cannot talk about their conditions. Anything you hear me present is strictly from the published literature as a way of correlating data.

Let me start off by helping you realize that we are not dealing with a synthetic polymer; it is not a melt. We are dealing with a natural polymer and, in fact, in terms of composites, you go right back to the source. You start with wood. This is cross-section of wood (Fig. 1). You have these fibers in wood stuck together. When you isolate any one of these tiny fibers and look at it, you have what they call a tracheid. It looks like this, about maximum of 2 1/2 mm long (Fig. 1). When you look at a cross section across that fiber that is 2 1/2 mm long at the outside, here is what you find (Fig. 2). Namely, you have Nature's composite. Wood is nothing but Nature's composite, and what is in there, essentially, is a number of different areas. There is a lumen (the cellulose layers) and a primary wall. In among the primary walls; holding them together and between the tracheids themselves, there are the glues (the matrix elements for the fibers). These are the fibers. The lignin and the hemicellulose are the matrix materials holding the fibers together in a composite sense. The hemicellulose is not cellulose, and it has nothing to do with cellulose. You do not want it, but it is in there, and this is the way Nature keeps the tree from falling over. The lignin is the structural glue that keeps the tree from hitting the ground, and the hemis do the same thing. In a microscopic level, you find that you have a layered structure in the fibers--the pectins or the different hemicellulose, the xylose, and the cellulose. Figure 3 shows the different layers.

We have 3 components in the wood itself and those are what we have to worry about when we chop the tree down. The first one is the hemicelluloses, depending on whether you have softwood or hardwood. You have a different type of hemicellulose structure. You will have a group known as

xylose or arabinose. The only difference between glucose, manose, and galactose is the positioning of the OH groups. These are very closely related, and all have different structural properties as a result of these OH relationships. But, the hemicelluloses are not good for you. They produce totally different burning structures. This is lignin, the matrix that you try to get out (Fig. 4). It is really a very simple building block when you break it down chemically. When this is oxidized, the result is vanilla. All of your vanilla flavoring in America is made from the oxidation of lignin from one mill.

At the pulping mill they try to remove these lignins and hemicelluloses; they depend strictly on the fact that these various components dissolve differently. There is something unusual about cellulose. More cellulose is dissolved at 0° than at 25° so that cellulose is more soluble in cold than in hot caustic. This point is important because you do not want to remove a lot of your cellulose. At 100°, some cellulose comes out, but it is a breakdown of the cellulose in the hot caustic; it peels out.

P. Pinoli That goes against the grain for chemical engineers.

A. Turbak Yes. That is very much so. It is very important to realize that cold caustic is far more effective in swelling and dissolving cellulose than hot. The whole trick to making a high, purity pulp is to control the conditions in the pulping. Nature provided us a DP distribution of pulp in cellulose. The S10 and S18 fraction comes out; S18 is lignins and hemicelluloses. The more dilute the caustic, the more it swells and allows more material to come out; therefore with a 10 percent caustic, up to 100 to 150 units DP of cellulose, pure cellulose, plus the lignins and the hemicelluloses, can be dissolved. With 18 percent the cellulose is not dissolved and a separation occurs. When pulp is delivered at S10 minus S18, this means two things: the mill is taking out the low ends plus the hemicelluloses at S10, and at S18, only the hemicelluloses are being extracted. This test can also be used on the fibers. The hemicelluloses can come out with an S18, which is not a problem (Fig. 5).

P. Pinoli How is the degree of polymerization actually measured?

A. Turbak They do that with a Cuene IV, but there are a number of ways. The one that is taken is to dissolve cellulose with cupriethylenediamine, which forms a complex with the 2-3 hydroxyl positions. Viscosity is measured in this manner.

J. Thomas What does the amount of caustic soda do for you again?

A. Turbak By your controlling the amount of caustic, the point of maximum swelling of cellulose in this curve is at or around 8 or 10 percent. At 10 percent, the hemicelluloses and the low

end celluloses are removed. Hemicelluloses are not celluloses.

J. Thomas Does that give you a better molecular structure or what?

A. Turbak It removes different levels of impurities. You do not want too many low ends left in there, if you can help it (Fig. 6).

J. Thomas Then what you are saying is that it gives you a better pure product?

A. Turbak Yes. Figure 7 indicates the purest cellulose you could have in terms of distribution. So, the whole trick is to take this impurity out without creating more low ends. The R_{10} is what remains (Fig. 5).

This is a typical, conventional Kraft paper pulp where no attempts are made to remove the low ends because the goal is to sell pounds. You have an unbleached stock in which you have basically the S_{18} (gives you the hemicelluloses); you see that that is a lower number than this (Fig. 6). The numbers of a typical Kraft pulp (paper pulp) run into this range (Fig. 6). If you purify that pulp, (dissolving pulp like that used for rayon) those numbers drop from 10 percent down to 4 and 2 percent, if you are lucky. Now, at 2 percent you have very pure pulp, but someone is paying for all the material that was thrown away, namely the rayon manufacturer (Fig. 7).

P. Pinoli But, that is an up-front charge for a viscose manufacturer.

A. Turbak Yes. He has to buy a decent type of pulp. Remember that I told you that wood is a composite with lignins chemically linked to cellulose, so you have to break them apart. There is only one way that you can break the lignins free--you have to have some kind of an acid-period of cooking to cleave the lignins from the cellulose and to cleave the hemicelluloses. You will find that there are only two ways to free the hemis. One way is by a sulfite cook, a fairly acid cook. You will find that you do make some pulp with a bisulphite cook, which is wide open, but it causes some losses; the other way one is to go to an alkaline cook for the prehydrolyzed Kraft. The straight Kraft merely means that sodium sulfate is added and then cooked. That will never cleave out the lignins, which is what you really want to do. Therefore, you steam hydrolyze it (put in steam and cook it up). Then the steam breaks off the acetic acid that is on the hemicellulose and generates an acid atmosphere in the cooker. This is cooked and the lignins gets loosened so that a prehydrolyzed Kraft gives a very nice dissolving pulp. If hemicelluloses and some of these chlorinated lignins remain in 1 percent, (they do not and cannot remove them all yet they do chlorinate them when they bleach the pulp). They build up in the caustic later on when you make the

viscose because you steep the first stage of viscose and steep this pulp to swell it. The chlorinated lignins are undesirable. During viscose preparation, they are sucked out into the caustic liquor which is not discarded because it is recirculated. It is important to see if these are in a rayon product.

In a regular mechanical cooking, paper pulp yields this much (Fig. 8). When you have the semichemical, at 50 percent, you get a bleached chemical in this range (Fig. 8). Almost 55 to 60 percent of your product is discarded at the start and is what the people have to pay for up front.

Figure 3 depicts what pulp looks like. A 2 1/2 mm fiber, magnified, shows all these lines in here. And this is what you are trying to dissolve. Then these are the cellulose bundles stuck together. The viscose process needed to make rayon depends on the use of cellulose (a 6-member sugar and a beta link). The 6th position is a little more stable in reactivity and a little less kinetically favorable (Fig. 9). In the viscose process, you are primarily taking insoluble cellulose from the tree, purifying it, making a soluble derivative by reacting it with caustic to make soda cellulose, and then reacting that soda cellulose with carbon disulphide to make a xanthic acid (Fig. 10). You are making a soda cellulose and then putting CS₂ in there so that you are esterifying the cellulose with CS₂. That puts it in solution. Then you mix an agent and after you filter it, you ripen it. When you ripen it, these xanthate groups (which were on positions 2 and 3), break off and either they go to 6 (which is thermodynamically more stable), or they go to by product by reacting with the caustic that is in the solution. Originally, a derivative is made that kinetically favors the 2 and 3 position, and when filtered then ripened goes to the 6. This is done so that if it does not go to the 6 position, you have a difficult time in coagulating and regenerating this goop. It must be ripened so that many of these groups move from the 2 and 3 positions to the 6 position, or it will not gel or congeal properly.

Herein lies the challenge of how to do the reaction properly. The first step in the reaction process is to steep in 18 percent caustic, which will remove all the hemicelluloses. Then that is reused. The pulp is shredded aged down to the proper degree of polymerization. You begin with at least 1000 DP and want it to be down to around 300 or 400, so you have to age it. Then CS₂ is added to the mixture and it is xanthated; it must be dissolved, filtered and ripened and the air removed.

J. Thomas

To what degree does the tree that begin with play in this? What is the source tree?

- A. Turbak It makes a lot of difference in their process if the source tree is hard wood or soft wood. The hardwood fibers are much finer; they do not have as much S₂ walls, and they drain differently so that you get a different build up of caustic residuals. It is a process problem more than anything else.
- D. Beckley Once you have a general classification of trees, and we think we are dealing with the softwood groups, what difference does it make if the trees are from Maine, South Carolina, or Florida?
- A. Turbak As long as you stay with softwoods, you will have the same type of hemicellulose and the same type of lignin because there are different lignins in softwood trees. There are more methyl groups in a hardwood tree than a softwood tree. It does not matter if as we were discussing 20 year old softwood in Maine or an 8 year old softwood in Georgia. I think in that sense, a pine is a pine.
- J. Thomas Can you have one tree or two different trees in the same family and clone another company's material.
- A. Turbak An individual needs to be careful not to mix hardwood and softwood, even though sometimes mixing is done on purpose in order to help the drainage, at this point. An example of why they do this is that if a mill is having trouble with drainage, they will put in 10 percent of a hardwood to help this drainage because that is the only thing that they can do.
- J. Thomas Say that you have company A that makes cellulose or rayon with softwood trees from Canada. Then you have another company that wants to clone that product in South Carolina, using local pines. Can that be done?
- A. Turbak It can be matched to a great degree.
- P. Pinoli The company will have to alter their process, temperature, time, caustic extraction, and whatever else. I do not think that everyone here has had a clear picture on that issue.
- A. Turbak The other thing that is important is that there are certain sequences of processing at a paper or pulp mill. The mill normally uses what is called a CEDED system (chlorine dioxide extraction on purification). When you chlorinate you chlorinate the lignins, if a certain indirectly has a strong chlorination step, then not only the chemicals in the chlorination step but also any chlorinated lignins that go out to the creek are undesirable. The mills are changing from the first-stage chlorination to hypochlorite, and most of the lignins and the hems are non-chlorinated. To the extent of heavy chlorination is used, much of the chloride

can remain in the pulp which will get worked into your caustic system.

P. Pinoli I am glad to hear you say that. I saw some evidence in the original work that I did on Avtex material in 1976 that indicated chlorine was present.

A. Turbak That could have been added as a chloride in the finish later but, basically it could be part of the lignin, too. You would know if you had the original sample before the finished extraction.

P. Pinoli I had assumed that they bleached the product

A. Turbak They bleach it at the pulp (several talking at once)

J. Thomas In the process in Figure 10, when do you know where you are with your viscose? How far along in the process do you have to be to determine whether you have the right treatment?

A. Turbak You will not know that until you get the fibers out. What you are trying to do here is to control the DP. For example, if I wanted a DP of 400, I would have to age it less. This is an alkali cellulose, loaded with caustic, I would leave it in there, in the little canisters, which is what the pulpers basically do to try to keep the CO_2 out. They aerate it; there is plenty of air in the cans and much depends on how long the AC is held. Fifty units would be lost later on when it is xanthated, no matter what you do. To get a 400, you would come to 450 here and lose 50 in xanthation. Figure 10 indicates where the CS_2 would be added, thereby making the xanthate. The extra caustic is squeezed out and then comes the dissolving step. All of the hemicelluloses and lignins remain in the process. If you find that there are too much of the hemicelluloses and lignins in the final viscose, then you are not dialyzing. You should dialyze the caustic before you use it for dissolving purposes. If you have more than 2 percent hemicelluloses, then you find that fiber will be rejected. The more hemis you put back in, the more brittle the fiber becomes. It does not perform. You cannot make a decent filament unless hemis are much less than 2 percent. What you want as a standard is 1.8 ± 0.2 , maximum. Then, after you have deaerated, all of this ripening is to prepare for the proper amount of coagulation when it hits the bath.

You want to xanthate at a very low temperature because this is an equilibrium process. Each time that you put on a CS_2 , that is called a degree of substitution, a gamma number. A gamma of 100 means that you have one CS_2 per glucose residue. A gamma of .50 means that you have one for every other glucose. You want to hold this as xanthate sulfur with a high gamma, but if you xanthate at a high

temperature, the same amount of CS_2 gives you a lower gamma number, by far, and more by-product sulfur. With 50 you get only about 18 to 20 percent by-product (trithiocarbonate), which produces gasses later on when you go to regenerate the fibers. You do not want to leave too much of this inorganic sulfur because that is not helping you to dissolve the fiber. The point is to get the xanthate onto the cellulose, not into by-product formation.

Figure 9 depicts what happens when you start to ripen viscose (that ripening process that rearranges the CS_2 from the 2-3 to the 6). You will make the by-product sulfur because some of these will go to by product, not always to the 6. It will hit a caustic molecule before it hits the 6 position. This tells you that there is xanthate sulfur in the final viscose as it spins, and it will start dropping as you leave it over a period of ripening time. The ripening time is in hours, so your viscose will change some. But notice what happens to your salt index (the amount of salt that it takes to coagulate this). It is easier to coagulate as the groups move from 2-3 to 6. The salt index drops. The longer you ripen the viscose, the more the xanthate sulfur will go to by product or to the 6 position less salt will be required to coagulate and congeal it. The top will be like jelly; the bottom will be a lot harder. Somewhere within the xanthate sulfur level, you will have a fairly easy coagulating viscose with a salt index of about 4 to 6.

P. Pinoli

How do they measure salt? What is the salt index?

A. Turbak

They use two salts--ammonium chloride and sodium chloride--and you need to delineate which one you're talking about. A salt index of 6 on sodium chloride is a salt index of about 14 on ammonium chloride. The ammonium chloride is not equivalent in coagulating capacity.

Now that we know that we have to coagulate this, we're not dealing with melts. Remember, you have at best a 9 or 10 percent solution, maybe less than that. You have 90 percent of water to be squeezed out before you can do anything to make a gel. You have jello that does not stretch. This means that molecules do not line up, so you try to get this as hard as you can by coagulation. You do not want regeneration because you still want that as a soluble form so that you can squeeze it and stretch it.

These are the 2 kinetics that you are facing--the kinetics of coagulation and regeneration. How you control these is a function of the remaining xanthate. If you have low xanthate, you will find that you will not have time to do much stretching; if you have high acid in the bath, you will not have much time to do much stretching because you have regenerated it. Once you get to the cellulose, you are just stretching jelly. You are still coagulating, the other one

and want to set up the thing until you get it to the proper amount. It is a well-known fact that the more salt you put into the bath, the more the dope congeals. That is where you want to be for the most part because the Jello will not do any good in making carbon fibers.

In making regular rayon, you ripen the viscose and put it into a salt bath at about 250 grams per liter of salt and about 10 to 13 percent acid and spin it. The end result would be a regular rayon. If the gel has a soft center and a skin on the outside, then the gel has not been totally "squeezed." As the gel started to congeal, it crenulated on the outside because the soft center was collapsing but the skin could not collapse.

P. Pinoli Is there a permeability difference between skin and core?

A. Turbak It is totally different because the whole structure was changing permeability while the acid came through from the outside of the fiber to the middle. It changed the whole diffusion nature every micron is a different field than the next one. This whole idea of keeping the inside from regenerating fast is an important part of the spinning process. It was discovered that if zinc is added to the process, then a zinc xanthate could be slower to regenerate than a sodium xanthate. Zinc was put in the outside bath. If a pH indicator (alkaline or phenolphthalein) is put into the viscose, that is skinned out of the nozzle, it is finally neutralized as shown in Figure 11. As this dope squirts out of the nozzle, it finally changes to where you get a change in the indicator color. You have a coagulation area and at this stage it's neutralized and you can forget coagulation from there on out. They said that they could put in a modifier with zinc and look at what happened (comparing Fig. 11 over Fig. 12) what you see is that the area of neutralization has moved from here way over to here. It has, in fact, slowed regeneration down significantly in terms of how long the system can live in the acid bath. This means that this time is the time of syneresis, squeezing out of the water.

D. Beckley Is that a crenulated filament?

A. Turbak Yes.

D. Beckley Are they both crenulated?

A. Turbak At this stage, both are crenulated only with zinc.

D. Beckley You do not have to take the water out of it to get the crenulation?

A. Turbak Ultimately you have to remove the water and still produce the soft center.

D. Beckley The water is still in both of them--90-10?

A. Turbak The Zn sample would have less water in the center because the skin is set up differently. Dimethylamine and polyethyleneglycol, which interact further with the zinc are added to the viscose so that it can congeal throughout. This is the way tire cord rayon is made. The interaction of dimethylamine and polyethyleneglycol with zinc provides all the time that is needed to make the hard center. This is all the reasoning behind the different rayon.

P. Pinoli Why do they need the hard center?

A. Turbak Regular rayon will dissolve when it is put into alkaline water like detergent. For example, if you bought a skirt or blouse made from regular rayon and you put it in the soapy water, then in 5 washes, it would look like cheese cloth. Soapy water is alkaline enough to dissolve 20 percent of the rayon. Consequently this is a poor quality fiber and has received a bad name through the years.

I want to introduce two new areas to you that are very important--strength and modulus. They are quite independent in rayon, yet, in a way, they go together because regular rayon does not have good strength nor good modulus. A modulus of 0.1 or 0.2 is nothing. A high tire cord will yield a higher modulus. Which, in turn yields a high strength. The reason is that there has been time to stretch the congealed gel, and the results are high strength and beautiful fibers. These fibers do not dissolve in alkaline soap anymore.

P. Pinoli Are these called high performance rayons?

A. Turbak Sure. It has good knot strength, among other things and still makes the best tires in the world. Michelin knows this and their tires have never changed because they still have the best resistance than any other tire on the road.

By controlling modulus and strength, you have a chance to do what typical technology tells you to do molecular orientation versus tensile properties. Condition tensile and wet tensile, and modulus (Table 1) go up rapidly and stretch comes in. Time to stretch the congealed gel affords greater increases in wet elongation. If I wanted to know how a man spun a particular fiber, I would never know from dry tensile alone; I have to know his wet modulus and I have to know the ratios. If you know how someone made a particular fiber just from running these tests and if he messes up, then the next time, you will know it because this test will tell you. You need to be more concerned with the test instead of how it was run. If the viscose has not congealed or if it was treated differently in that initial zone, you will get totally

different ratios of that dry tensile and of elongation. It is very difficult to make a fiber with less than 15 percent wet elongation, even the high wet modulus modal fibers. All of these tire cord yarns have 15 percent wet elongation. An Avtex fiber has 9 percent. We need to question what is different. Avtex has an elongation of 9 percent wet; consequently, it should have a tensile of 7 grams. It has 3. Something is different here.

Figure 13 depicts this ratio of wet to dry tenacity, changing with percent stretch, which is to be expected. During this stretching, these chains are being put close together and some hydrogen bonding occurs between the 2 and 6 position, and so forth along the chain.

- D. Beckley Is there a hydrate of water in that structure?
- A. Turbak Initially there is, it disappears when the chains come closer together on drying. When cellulose is dried the same structure is never achieved. Once a wet-gel cellulose is dried it will never return to reswell. New bonds of swelling are formed in new pores, which are much bigger. These pores are like tiny trap doors. If the cellulose is swollen in a swelling agent, even in water, and is put in carbon tetrachloride or chloroform, then collapsed, the chloroform will not be removed even if it has been put in an oven. It will come out when it has been rewetted. Some of these parameters are this critical.
- P. Pinoli What intrigues me is that you are looking at the rayon microstructure; I am looking at activated carbon, and we see the same characteristics.
- A. Turbak If you want activated carbon, then you take cellulose, never dry, and swell it. Do not dry it, but displace it with a solvent. You keep the swelled pores open, carbonize it and then you will have 5 or 10 times the unit you had. Fig. shows the corner of the crystal which can be defined. Hydrogen bonding takes place at the top of the crystal, between the chains, and along the chain; you see some of these naturally between positions on the chain coming in to hold the crystal together. You can run a crystal in to the diagram on cellulose and if you have a totally amorphous structure that has never been, crystallinity comes from stretching; it does not come from congealing. This is the way the pattern would look for the different planes (Fig. 14). Figures 15 - 17 depict where the planes were. This is the one-on-one plane that describes which way the x-ray is looking across this crystal.
- P. Pinoli When you stretch this material, are you causing these fibers to get close enough to induce hydrogen bonding?

A. Turbak They start to crystallize. You do not want that for your carbon fiber. Tire cord should be absolutely worthless to you. (group discussion). You have a totally amorphous structure made by using hydrazine as the dissolving medium and spinning it. If you take regular stretched cellulose like mercerized cellulose, then you see that you get these levels. A pure cellulose made by hydrolyzing stretched acetate is a densest medium. When you pull it under a little heat, stretch it, and then hydrolyze off the acetate groups, you get tremendous patterns of crystallinity (mercerized cellulose). Your material, incidentally, does not look anything like this. What you get from Avtex through courtesy of Huntsville is old Avtex and the new. There is no difference from this because it is not that good a discriminating factor, I guess. Basically, this is very amorphous, and you do not have sharp peaks.

D. Beckley Is that the 002?

A. Turbak This is a 21 degree angle in this part of the 002 plane. A year ago, some fellows said that we could look at some of the parameters in spinning. They showed us how we can make cross sections and stain them with Victoria Blue to see the skin versus the core. If you take all of these different rayons that are available, you will see that this is regular rayon here and B is a low-wet modulus. You see a little more skin by delaying the regeneration by putting in zinc. You get all of these by putting all the way up to a pure run cross section, no crenulation. This is the old Avtex; the new Avtex looks like it is in the ballpark of where you want to be, 20 to 25% skin in both cases.

P. Pinoli On that procedure, how sensitive is the dyeability procedure to assessing skin/core condition? You dyed the fiber and then introduced alcohol, to leach it out, and what you are really doing is looking at the retention of the dye in certain areas as opposed to the others. Is it possible that you are fooling yourself a little bit with this technique?

A. Turbak No, the desorption is fairly fast. You will lose it about this fast then it will level off very slowly after that; they recommend about 5 minutes to leach it. The technique was proven pretty well. An intense study of all the rayon that was on the market before it was published showed that the spinning the rayon is related to structure. It is old data, but it is the basis upon which the test was based.

Table 1 shows at this modulus how these fibers compare with regard to strength. We have a high-wet modulus rayon that is strong, with low elongation. If you take 2 1/2 grams of a regular rayon, number 6, wet it, it stretches like it is already at about 25 percent stretch. This is 35 percent stretch and the strength drops down to something like 3.6. You know that you do not have much structure. If you take

the one that is a high-wet modulus at 7 1/2, it drops to about 5. It is still a very strong fiber and in terms of stretch, it has 7 1/2 grams and has only 9 percent stretch. When wet, it is still up to at least 10 or 11 percent stretch. Yet, you are dealing with a fiber from Avtex that is 9 percent wet stretch. In other words, either you should have a very strong problem with stretch or something because this is something entirely different.

We need to look at what they are doing so that we can find some reasoning from what we know. I have gone through numerous books and looked at every rayon fiber that has ever been commercially made from rayon in the world. By looking at some of these conditions, we can see that the condition and wet tenacity and the conditioned and wet elongation makes it very hard to find a fiber with less than a 10 percent wet stretch. Avtex has 9 percent stretch, never more than 10, roughly. Conditioned 3 grams, and when it is wet, it goes to 2; your fiber is about 3 going on 1 1/2. I do not think that you have 2 anywhere. (group discussion)

You have a very weak wet fiber, yet it does not elongate. In general terms, wet tenacity versus stretch; tenacity goes up with stretch; elongation--it goes down a little bit, but is still up there at 11 percent.

It is not easy to get, even with formaldehyde, a wet elongation that is this low. It is a very tricky system that does that. I have filed a patent on information about such a system. You have a weak fiber. This is a problem with the way you are running it, conditioned versus wet. This is very close to the Avtex fiber, but your elongations are quite different from that. When you come up here, you get the high wet modulus, and you end up going from 7 to 6, 4 to 3 (Fig.), which is too strong. The whole thing is off balance.

Years ago, Joe Alexander, a member of one of the groups I had at Rayonier, was in charge of analytical, and he developed a test. We decided that if this fiber that you make regular rayon from dissolves so much in just regular alkaline wash water then, that ought to tell us something about the structure. So, Joe made a number of tests of different strengths of caustic, and it turned out that at 6 1/2 percent caustic at room temperature, you can get a very nice discrimination of all kinds of fibers from rayon. He ran hundreds of them; everything that was on the market, he ran. Joe found that caustic solubility at 6 1/2 percent caustic at room temperature, related quite directly to this wet modulus we have been talking about. When you have a wet modulus of a high strength fiber, 1.6 and 1.7, you have almost no caustic solubility. Avtex fiber is right in here (Fig. 18). Avtex fiber with about a 4 to 6 or 7 percent should have a wet modulus of 1.2; I do not think it is that high. This is

intriguing because it says that now, we are starting to see modulus as relating to density of packing and not necessarily stretching. I am separating the two as I did earlier. Joe found also, that it is not a function of cuene l.v. because with the same l.v., he could get S₆₅ all the way from 8 to 35, depending on how that rayon was spun.

I have argued that densification is related to modulus, whereas, strength is related to stretch. This has become so prevalent an argument within the group that I was with that we decided to do something about it. We generated some data which eliminates such arguments, at least with reasonable people. Rayon fibers having a high wet modulus, a low wet elongation, and low caustic solubility are prepared from an unmodified, no zinc viscose spinning system by spinning into zinc-free coagulation bath with extremely high salt and low acid at a low temperature. This is very interesting. This is supported now by some data (Fig. 19). The unique control capable of being exerted on the spinning process is evidenced by the resulting fiber properties. S₆₅, with solubility in caustic, is an important property because it measures the fiber resistance to dissolving. By the process of this patent, it is possible to have fibers with an S₆₅ as low as 3 to 5 percent. Regular rayon is around 20 to 30 percent. Fibers with such a low S₆₅ previously had a formaldehyde content, and the reason that the S₆₅ is deemed to be that low is probably due to coagulation as it is densified throughout the fibers before being regenerated in contrast to regular methods. Namely, if you take the time with a high salt in your bath and proper viscose to totally squeeze everything out of it, you will get a fiber that has low elongation, not high strength, because you are not stretching it. Your conditions are such that if you try to stretch it, it will break, and this is about where I am predicting that Avtex is currently operating.

Condition tenacity, 2.31; condition elongation, 8.16; wet tenacity, 1.5; wet elongation, 9 percent. I bet Avtex is around 1.5. On some of these, you do not want high strength. You want low values and the reason is that this is a kind of viscose, 7.77/7.5/30, that would be used to make a good high quality fiber yet this is not a high quality fiber. We also ran experiments with a viscose that they used to make a lower quality fiber, and it works fine too. Mainly, the conditions are what are important as much as the viscose, and this second viscose was prepared from a lean viscose of almost 9 percent cellulose, 6 percent caustic, and 28 percent CS₂. This is a very lean viscose. The properties are as close as what anyone will come to matching Avtex any time and it can be done without zinc; even with zinc, it gives you a little bit stronger fiber. Dependable data, deters disaster and I think that this is fairly dependable data.

P. Pinoli

Is it strictly cyclicalization?

A. Turbak

In the case of the acrylonitrile, The first step is an imine formation between adjacent nitrites. You start making the second step which is that you have the carbon from the next ring and you remove these nitrogens; the carbon comes into nitro and makes your graphite. If you compare that with cellulose, you have a ring that looks like this. To make this into graphite, you have to blow out 6 moles of water to make this carbon come over to where this oxygen was (Fig. 10). You need to have room to move. You do not make good product if you have crystallinity so you have to have a chain density where you have a close approximation but no crystallization. That means high or good wet modulus, close packing, and that you will have low caustic extraction in the Avtex fiber. It is also the reason that you will find low elongation because you really have a weak fiber. If you start to stretch it, it will break because it is so stiff in terms of a hard center. This reflects itself also in shrinkage. When you shrink the viscose, you swell it and allow it to collapse. If you still have jelly in the middle, it will collapse and shrink more. If you have jelly in the middle and you let it come down with no tension, it will shrink a lot. If you have that fairly densified in the middle and swell it, it is not going to swell or shrink as much, so that densification of the center is important to you. One of the things that is not on this list of properties and should be is the hemicellulose level.

(Tape was changed here; didn't pick up the start of what F. Turbak said)

You do not want a lot of skin. The important thing is not conditioned strength, but the ratio of tensile wet to conditioned. You want to know the wet value which is more important to you than dry value because that ratio should be in this league here (Table 2) to show you that you densified that center. The elongation conditioned should be no more than 7 or 8 percent, (I show 7%), and it should not become a big number on wetting. These can go over by 60, 70, or 80 percent when you wet many of them, but if it is dense inside, it will not rewet or reswell like a balloon, neither will it elongate wet. That wet elongation is a function of densification and stretch. The wet modulus (what they measure that 5% elongation) should be around 0.5. The rewet swells. This is something that you do not do now, but that you should do because this will tell you something about how that product will densify. You wet it and centrifuge it for about 5 minutes, and you know that if it has picked up 100 to 200 percent water, then you have a jelly. Whereas, if it picks up on 50 to 60 percent of the water, then you have a nice, hard core in the middle of it, and that is what you are looking for. You do not want a lot of skin; you want that hard middle.

In moisture regain, this is also the same type of measurement. Typical rayon would be about 12 to 14 percent. If your rayon is hard in the middle, it will not be more than 8 to 10 percent and it should not be more than 9 percent. In the cross section, (Fig.) should be crenulated with about 20 or less percent skin. At S₆₅ this is a little dissolving thing that I think is important and it should be less than 8 percent or you will not have that densification in the middle. All you will have is a lot of skin on the outside, but between this one and this one (Fig.), you will know what you are dealing with. I can take any fiber and tell you if it will be decent for your product under these conditions which I could not under other conditions. The knot strength is something that is very critical. No one seems to worry about it because usually a fiber will lose at least one half of its strength in its knot. It does this because when you bend any material, the outer surface will be in tension and the inside will be in compression. It is easy to measure tension. The way to measure compression is to measure your knot; the inside of the knot is in compression, not in tension, and if this is not right, then you will find that the knot strength is quite different. And if you have a high strength fiber, then the knot strength will be much less than 50 percent of the conditioned tensile because it is so strong in the conditioned and the knot is so weak, brittle, and straight, it is more like a hard spaghetti that will crack on you in compression faster than typical rayon. You want something that will do all of these. The pH should be above 5.8 but less than 8.2 because if it is less than 8.2, then it is alkaline, and it also means that someone did not do a good job of getting rid of the xanthate sulfur.

- P. Pinoli I do not understand how you can have a pH spec range from 5 to 8. I would think that there would be a favorable side: acid or base side of 7.
- A. Turbak You can leave it at 7.2. I do not want it on the alkaline side. I want it between 5.8 to maybe 6.5.
- P. Pinoli That is one thing that has bothered me about the acceptable pH allowable extending from very acid to nominal basic.
- A. Turbak Eight is too far. (group discussion) I would like to see this at 6.8 to 7. It means that they have done a good job regenerating and washing out the acid. The problem is that some people might like to neutralize that acid, and if they do that, they will overneutralize. You can wash acid out of cellulose, but you can never wash caustic out of cellulose. If I treat cellulose with caustic and put it in any running water for the next 15 years, it will still be alkaline when I come back. This is like acid out of wool. You can take alkaline out of wool, but you can not take out acid. It is very difficult to remove alkaline from cellulose. Usually, to

get rid of it in the textile process, you neutralize it after the washout process. With regard to shrinkage measurement, they put 4 grams.

- D. Beckley I believe that was 4 ounces, 1/4 of a pound.
- A. Turbak They put this weight to straighten the fiber, wet it, put it in an oven, let it shrink free, and then measure it again. If they get a jelly center, it will shrink more, so they want to be under 3 percent on that. This is a measure of how well they washed out the sodium sulfate and other impurities. You do not want any more than that. Zinc should be less than that (Fig.) which is a very generous number. Sulfur should be as low as possible; they will have colloidal sulfur in the bath, which I do not know the effect on carbonization.
- D. Beckley I have never seen any detrimental effects on that. In the amounts that we have left, we do not have a problem.
- A. Turbak This could also represent residual sulfate which is inorganic. That I would worry about if you should determine this, then the sulfate should be a very low number.
- P. Pinoli When I look at the sulfur, I question what form it is in, sulfate or xanthate?
- A. Turbak To make fiber free of sulfur, fiber will have to go through a sodium sulfide extraction or chlorination which would leach sulfur out. That is the only way they know how to get it out. The colloidal sulfur is very hard to remove.
- P. Pinoli No one is going through with desulfurization, are they?
- A. Turbak No, not that I know of. That reswells the fiber. Once that is done, you put in sodium sulfide and the fiber swells up like a balloon and all this work that you did to densify it has gone down the drain. Cobalt is one that I have put in on my own because cobalt is one tremendous catalyst to cellulose degradation. One part per billion of cobalt will cut down the DP faster than 100 parts per million of manganese. Look at the trace elements in terms of messing up your results on conversion to carbon fiber.
- P. Pinoli What about lead?
- A. Turbak Lead is not bad; it is nothing. Iron, in fact, turns up. Copper is the one that helps you. Copper is ??? you won't lose your DP as fast if you use copper. Manganese and the transition elements, in general, are active catalysts.
- P. Pinoli Is that where the Copper number comes from?
- A. Turbak The copper number is a measure of aldehyde groups, if you have aldehyde on cellulose, you treat it with a copper

solution. The aldehyde gets converted to an acid while the copper is reduced, and you use that copper precipitate to measure the aldehyde. You do not want any chloride in there. If you have some, it is because someone is putting it in or because you did not wash out all the chlorinated lignin. You want that very low. The finish is really up to you. You do not need a lot of finish to weave. The polymeric finish is to hold the two turns of twists that are in there and if that is done correctly, then this will give you some lubrication. The main thing to remember is that you will gain by putting in tests for a wet tensile and its ratio and wet elongation. The wet figures of this reswell value is a very important part; the S₆₅ that you are not doing anything with right now, will give you a lot of data if you follow that. That is quite a balance of a lot of properties.

- T. Bhe Dr. Turbak, how does the higher wet elongation value affect the spinning process or does it affect the spinning process at all?
- A. Turbak If you get wet elongation that is very high, then you have not densified that center, which means that you will have a lot of jelly in there. You will not overcome it because you do not have the skin; you don't want the skin (See Comparative Data Figs. 20 - 21).
- T. Bhe So they can continue to spin it to get a lower value of wet elongation.
- A. Turbak They can spin this to make this value low, and they do it by causing that congealing in the initial few seconds.
- J. Thomas Dr. Turbak, I think I heard you tell us that you would not go and clone the Avtex rayon.
- A. Turbak No, I did not say that at all.
- J. Thomas Well, it was pretty close to it.
- A. Turbak No. I said that if I wanted to clone the Avtex rayon, then this is the way that I would approach it. Namely, I do not know what Avtex is doing, and I do not want to know what Avtex is doing and will not say a word on that. This is nothing but literature. If I wanted to make a fiber with low elongation, which is the trait of the Avtex rayon, this is very unique. But Avtex rayon is unique in that it has a low strength fiber with low wet elongation and low S₆₅, which is a total dichotomy. The only way you are going to get the fiber is not to spin in the regular sense of making a spin with high stretch, but to spin really by precipitation early in the game. One of the characteristics of such a process is to have a low salt index so that it is ready to flop out. If you have a high salt index the elongation will go right

back up. You have a lean viscose with a low salt index; and you spin that in to a high salt bath with low acid thereby causing this to precipitate out and becoming very hard set.

J. Thomas If you were designing a rayon yarn, ?????? designing
(inaudible)

A. Turbak I would not design this for any other use but yours.

J. Thomas That may be very difficult to process, but it works.

A. Turbak This is very difficult to spin. If I had to spin this yarn, it would be a challenge. There will be a lot of waste in spinning the yarn because there is not going to be enough xanthate left for me to stretch it. I would have a difficult time spinning this.

J. Thomas That is why they are struggling with yields (group discussion)

A. Turbak That is exactly correct. Without the zinc, they would not even make it. [The zinc gives them a way to get down the machine.] You will find that it is not a high stretch yarn. My prediction to you is that the secondary bath stretch is no more than 80 percent, which is very low for a viscose.

B. Hall We have about 15 or 20 minutes more before we will be through with this part of the program; do you want to take a break now or do you want to continue?

M. Towne Lunch is ready, so let us pick it up after lunch.

LUNCH

B. Hall We will pick up where we left off, talking about the second source for our rayon precursor. Next on the agenda is Don Beckley who will talk about the Navy's interest in this.

D. Beckley I would like to try and pick up the story where this group was at its last meeting and briefly carry you to, probably, where we think we are today in the rayon business. I must say that what we want to accomplish today is to tell as much of the story as we can without inferring or using any of the Navy Lockheed D-5 rayon program material. So, I caution all of you to help me not utilize part of the program that we have been collectively working on for the last 2 months as the first line priority. The reason for this is fairly normal in Navy program pilots; they like to reserve the right to review data before it is presented, and obviously we are dealing with things that are so new that there has been no opportunity to make a presentation to Lockheed of what would be presented here. I will attempt to make this a non-D5 discussion, and there are times when we can ask each other questions to make sure what we know is

not D5. I may resort to that technique. At any rate, let us roll back the clock to where we were, and I guess, mid-December or late November.

We were sitting in the meeting, knowing that only part of the funding that was going to be required to get Avtex restarted was available. The DOD portion had not yet been made clear, and ultimately, that has come along. What has turned out is that Avtex has received an injection of money, \$38 million, plus another \$5 million, for a total of \$43 million.

We will cover a little bit of that story event. Avtex was down physically as a plant for about 6 days, but by the time they got back up and going, and we looked at our receipt requirement, we were about ???? on rayon. Things since then have gone, I think, much better than most people, almost anyone, imagined in terms of their quantity of material that came out of the plant based on their restart schedule and based on the indicated characteristics and quality of that material. We have mentioned several times that they do not have 100 percent yield; the evidence is that their yield is probably better than they were making before they shut down. The first materials have actually gotten through. I guess that nearly the first 50 thousand pounds of material is in carbon form now, and no one has a mark against it that says that it will not be normal and working. This would be a story that was appropriate to tell as of last week or maybe the week before. As usual, there were some concerns, some worries, and some risks about Avtex and their surfacing at this hour in 2 forms that may affect this group in the way its headed in function. One is that the State of Virginia had arrived at peace with them on an environmental recovery plan which included a certain amount of money that was set aside of the \$43 million and that was going to fix some of the environmental factors; consequently, there would be relative peace in that world. Sometime last week or just prior to the week before, the State filed another suit against Avtex. The suit extensively says that the zinc level in the Shennadoah River is not satisfactory. Sitting here, we can not judge whether it is really worse than it was or whether it is the same and this is something else. The implications are certainly a concern for people who are counting on the Avtex restart and continuation. As they shut down, they had 9 machines on line, and these 9 machines were capable of producing the amount of rayon that the industry was requiring, roughly 2 1/4 million pounds per year. As they have come back on, they have been asked to increase that amount of production and are currently up at the 20 machine rate. You can mentally see that we are able to satisfy ???, and this has been the joint plan of both the NASA and the DOD type operations, to get ahead on rayon. Avtex is providing us the capability of getting ahead to the tune of about twice as much rayon

as we need to assimilate into their programs, so part of it goes into a stock pile on the agreed-upon ratio between the NASA and DOD programs. They say that everything would be fine, but for the proviso that Avtex is successful in correcting what the State of Virginia will require of them to do about this element called zinc. Dr. Turbak has certainly helped us understand where this zinc comes from in his discussion today. There is another factor that is even more nebulous, and I am not going to be able to dwell very firmly today on it. The \$43 million that was put into the thing is apparently coming close to being consumed in getting the plant up and running. Carbonizable rayon is not the problem; the problem is what caused Avtex to shut down to begin with. They have a commercial business, making staple rayon to the tune of roughly 150 to 160 million pounds per year and roughly 3 million pounds of industrial. When they shut down, some of their customers who buy staple did not remain loyal. The quality of the material and the staple is apparently somewhat of a ????, and they are not selling all they can. They have a negative cash flow position. Now we do not have the visibility of being certain how long that operation will be able to continue. I want you to be aware that there are certain clouds on the horizon with Avtex. What they are producing today and what is needed is several, actually many more months of production before there is a safe amount of material in anyone's inventory. For the good of all of us and the wisdom of a government that gave them the \$43 million, we certainly hope that that continues. It will be tough if it does not.

One of the alternatives that is going on is pan qualification, and this group is involved with SPIP's version of that. There was an effort that was started by the Navy then stopped. We do not expect any more action out of that area. The third pan activity that is coming on and probably will be the first to rise or fall has to do with the decision to attempt to consider a replacement of rayon in the Titan 4 upgrade program within the near term. This program is new, and now is an opportune time for designs to proceed into development, one in rayon and one in pan. If you look at that program in comparison to SPIP's supporting ASRM, you see an interesting contradiction that we will all work with. SPIP has planned to run maybe 4 1/2 years, maybe compressed to 2 years; this is another program that is designing, building hardware, and installing, a program that is really going to have to make some decisions within the next month on material utilization, parts, and hardware. They represent an interesting thing like our industry, old and new. When we did not know what the next rocket motor performance was to be, we looked at the last one. We guessed. The best thing that we could do was to build a part and fire it, and if it worked, then we knew that. Then we went on from there to build another one to go. That is how the Titan 4 U program looks; it is a very ambitious, certainly a risk-taking

program. There stands a possibility that pan will enter critical nozzle components early. They will do it. In contrast, SPIP says that we are going to take 2 1/1 to 4 years, and we will get all of the data we need to design every component. We are going to do everything to know about the material. We will have a sufficient data on rayon vs pan each step of the way. We'll know why it works and things will be the way NASA does them. I think that, as a group, you can look forward to seeing those two activities and watch the maturation of them.

The other alternate to Avtex is alternate rayon qualification, not alternate pan. Last November, NORC (North American Rayon) was identified as the only domestic source making continuous filament rayon besides Avtex, so they became the logical alternative source for the material. They spent 2 months attempting to explore the envelope of the spinning process that Dr. Turbak talked about today. They made what is known as 18 variants--18 different kinds of rayon. This rayon represented what they thought of as a statistical control experiments. The resulting materials came out with combinations of strength, elongation, and shrinkage--3 critical parameters, none of which collectively matched the 11 criteria that go into the current rayon spec. In general, they produced a material that had the equivalent amount of strength for slightly lower in strength. They produced a material that Dr. Turbak indicated is more normal than the carbonizable and material, that has a shrinkage, or elongation that is higher than the spec limits. In turn, the shrinkages have tended to be greater than the spec limits. In the parlance of things, they did not achieve a clone, and I believe that later on. Lou Anne is planning to speak of things that are coming on in that area. We have not had a chance to coordinate, so I will just drop it there, and we'll expect to hear more of that aspect.

One of the things that I think is relatively unique about the way the situation is is that NORC is definitely interested in the business; to them it makes sense and they are willing to go forward., The space shuttle program made a commitment to North American that said "If you will get into the business and if you can get qualified, you will be entitled to about one half the business henceforth." If that had not been done, they would have been sitting around, looking at 100 or 200 thousand pounds of potential DOD business, and we would not have any opportunity at a second source. We would all be very nervous about \$3 billion industry that was going to shut up and close down because of the lack of \$5 or \$6 million worth of rayon. There is a tremendous leverage factor from that sole source position that some people had quizzed them to basically effect, and it is fairly safe to say that we all have a stake in making sure that we get the second source .

Hitco has pretty much generated some information which on its own gives a slightly different slant, but in general, agrees very well with what I heard coming from Dr. Turbak this morning. Our activities concern what works as a carbonizable rayon resorting both to past information, and to some relatively near term current looks. summarizes that active

This is tensile strength (tenacity), but it is in pounds of load that is put on a 1650 denier yarn, and that is the principal of rayon yarn. It is used except for the 1100 denier that goes into some of the Amoco products. This is the elongation term. The square block in Figure denotes the spec range for carbonizable rayon. The spec range here pretty well limits the upper end of what is probably achievable, and it separates low, intermediate, and high strength rayon. The high strength areas are generally called tire cord. That material does not make a carbonizable product. If you recall, that material contains 1 or 2 different additives that are not favorable to carbonization. In essence, that product does not work. We have looked at it not only in the past but also in recent times.

We have f3 convertors ??? , Polycarbon, Amoco, and Hitco ??? , and each of our processes may be slightly more sensitive to one aspect or another. But they are all relatively long term fabric conversion processes. It takes anywhere from 8 to 12 to 14 weeks to get through the processes and we needed an answer in shorter lengths of time. Polycarbon has a commercial process that provides a shorter view at things; Hitco, in their efforts, created, essentially, a two-day process, taking 12 weeks and cramming it into 2 days. In this process, we basically used Avtex as the reference material. When we could get Avtex material through the process, it was created in a short time process, we said we had a discriminator. At least Avtex would work. We took tire cord and put it in the short term process and it did not work. Historically, we put tire cord in the long term process and it did not work either, so we probably have a pretty good reference to the fact that none of us expect tire cord to make the grade.

We've had an opportunity to look at a number of materials that fall right around this level in Figure ???. They have about 10 pound strength in a 1650s yarn, and 10 pounds times 454 grams gives you basically, very close to 8 grams for 2 1/2 grams of denier of material. What we have tended to see is that in this short term process, where Avtex would make it, if we put rayons in that are lower strength than the equivalent of the 10 pounds, they do not come out of the process. We need a 10 pound yarn strength to get about 1 pound (450 grams) of load carrying capability to get through the short term process. It almost looks like the lower spec limit for carbonizable rayon is sort of being described by

process requirement on the carbonizable side. We would really recommend that things which are lower than that are probably not going to make it. The favorable thing that we have seen, though, is that you can move across from this elongation line into this area, and you can find materials which are coming through the process (Fig.). I am certainly not in a position to say that we recommend going to a higher elongation, but there is evidence that materials of a higher elongation will work. Figure donates this. VCW is villwite. Villwite material was a 14% elongation material and was the material used before there was an Avtex. I have researched it, and the specs allowed higher elongation at that time. When we went to Avtex and asked what they made, they described this block right here (Fig.). It is carbonizable rayon today, but there is evidence that in current time, we may be able to live in this area and there is evidence that we did live in that area in the past.

- P. Pinoli Don, do you have the specs for the Villwite material? I have asked many people about that and they have assured me that one existed.
- D. Beckley We have access to a bunch of villwite data that has not been fully assimilated.
- P. Pinoli Accesses to the Villwite specifications would help all of us.
- D. Beckley I recognize, I think, that there is some importance to it and that some more work has to be done before we can do that. We are confident that much of the QC data shows this kind of elongation for villwite; it also showed that there was an awareness, surprisingly, of a need for a void-free filament. They knew of the presence of crenulation before there was an Avtex. There is some fairly recent information, yet on the other hand, I think that what we have come to see is that we have NORC setting there and they have their equipment and are going to have to make rayon, to an extent, their way to get it. There is no use in saying "If I knew exactly how either x or y stretched the material, when you go to North American, that is exactly the right amount of stretch. Their equipment and their process is going to make it their way, so having a complete description does not really give you an answer except for the fact of what has helped.
- P. Pinoli What is strange to me, Don, is that I looked, back to the time when we qualified Avtex originally, and I find no previous specifications for rayon.
- D. Beckley Well, I do not even have my numbers here. I have been told that there is a spec, and I think that the archives will produce them eventually.

This is only pertinent from the standpoint that crenulation pictures; this is the percentage, 5 of 6 in 8 of 70 filaments with folded in crenulation. This was material, which was in essence, late 1977 Avetex material and here was the 1985 material with 26 over 60 and 34 over 60 (percentages for folded-in crenulation). We know that we can live with both, but there is certainly an interest and a desire to have that particular crenulation maintained with as few holes as possible. There should be some way of getting that property as well as the additional things that Dr. Turbak showed us this morning.

We have pan under way; we have rayon under way. Lou Anne will later close up what the next step would be. We have a little more risk that we were worried about this week with Avtex, but it was inevitable.

- D. Herman Don, did not we put villwite in C3?
- D. Beckley Yes.
- D. Herman Why do not we just go to our old files and dig up the information?
- D. Beckley We can all dig the prepreg data back to fabric data, with no problem. I am not sure that what we will find is incoming certification data essentially passed on from the weaver who was, quote, "Burlington," at that time, or what was required of them. The first real record of things stems from a spec that Hitco wrote early in the Avtex days and has, frankly, been transcribed by everyone in the business since then. We have all decided to use the same specs; the thing has become a ground rule. It is a little nebulous right now. We used villwite from 1963 through 1970.
- D. Herman I would say 1974. The C3 production program was in 1975.
- D. Beckley That was all villwite. The characterization level as you go down stops at the fabric level--a carbon fabric. Even today, the only specs that exist below that are the specs that I was reflecting which was the Hitco spec that has been transcribed with other designations on it.
- P. Pinoli I do not think you will find any records, Dick. Those control specifications had no visibility at your level. Burlington is the only possible source of IRC data.
- A. Turbak Was Inca supplying you, too?
- D. Beckley Inca had a very short history. We laid in an inventory of villwite. They announced that they were going to shut down, so there was inventory bought ahead. Inca came on stream and then essentially went off stream, even before they got

out of the development phase. There was very little Inca ever made apropos.

- A. Turbak It was my understanding that Inca taught Avtex their process. I think that is a fair statement because I know the people involved and that was transmitted to whatever Avtex could do on their machines with the Inca recommendations. That is what was developed.
- M. Towne We were looking at both Inca and American Viscose at the same time together for our high modulus yarns. We converted to Inca, but never converted to Avtex.
- D. Beckley Is that for the fornell rayon yarns that we are talking about?
- M. Towne We may very well have some records of the time of the conversion to Inca. We did the conversion.
- D. Beckley Once again, what do you think you might have from villwite days?
- M. Towne I am sure that we have a lot of old information on villwite because we were working very closely with them in Cleveland. I do not know, how much of that is retrievable at this time.
- D. Beckley Now it is not critical, but I think that should there be a larger upset at Avtex, it may become very important. Lou Ann will later tell us the story about cloning. Just looking ahead, if they are not successful, and I am not really in a position to make a judgment on that, I think that it is important to the industry to know that we use something quite successfully that was not a clone years before. So, that is really the message for today.
- J. Thomas Don, you have to remember that if Avtex closes its doors before they deliver the 1 1/4 million pounds, NASA has the data banks to the Avtex process. That is the key right now; the first week in July (inaudible).
- D. Beckley Jim, I think that it would be helpful, data wise, but in all honesty, I think there are several Avtex graduates from the University of Avtex who are in the industry that North American has already had access to and who has not made a clone. There are many of things that are yet going to happen, but I am not too sure that there is a whole lot of value that if you had a recipe book, there is something that we collectively do not know.
- J. Thomas Maybe the recipe book has that data.
- D. Beckley Yes, there could be very neat little books.

- L. Fikes Is D5 doing anything with North American Rayon to get them on line? Or are you just waiting to see what NASA develops?
- D. Beckley I am going to be careful and say that this is a question. That is the safest way to leave it at this time.
- T. Bhe There are certain modulus that is carbonizable, and you mentioned that this is based on carbon from the supplier.
- D. Beckley Ten pounds breaking strength and 10 percent elongation is carbonizable.
- T. Bhe You also mentioned that villwite might work.
- D. Beckley Yes, villwite is the material from the early 1960s. In the early 1970s and 1974, 1975 worked with a 14 percent elongation.
- T. Bhe Did someone do the analysis on the 10 percent or is there a cut-off point?
- D. Beckley I think that we are all saying that as carbonizers, we do not know exactly what makes carbonizable rayon for sure. I tried to say today, I think, that we know a little bit of what the bottom limit is made up of now. We do not want to be below 10 pounds because our processes just do not respond to it. We know that we do not want tire cord material even though it is much stronger, and that is about the upper limit. Maybe what we can do is work the elongation range wider than the spec which is the Avtex material--a greater degree of freedom for what we will work.
- B. Hall Thank you, Don. Lou Ann will continue our program.
- (D. Beckley and L. A. Fikes talking--L. Fikes asks about the D5 and Beckley responds with "anything that NASA knows, is okay. It's just people who....")
- L. Fikes I am Lou Ann Fikes and I am here today to tell you about NASA's efforts to get North American Rayon on line as a second source supplier of carbonizable rayon. We know we have Avtex, but do not know how long Avtex will be around so we have gone to North American Rayon in Elizabethton, TN for our second source for carbonizable rayon. These are the requirements for the SRM carbonizable yarn (Chart #2 of my handout). NASA uses a 1650 denier so the specification requirements that you see here are ash(45%), sulfur, .25 percent, zinc is .07 percent, ph is in the range of 5 to 8; finish is between .2 and 1; twist (turns per inch) is in a range of 1.6 to 2.4; break strength is between 10.3 and 13.5; elongation is between 5.5 and 9.5%; moisture is 13 percent max; denier is 1650; and shrinkage is between 2.9 and 4.7.

As of March 31, 1989, North American Rayon has completed the following carbonizable rayon development. As of March 31, they have had 18 experimental runs. They changed the spin bath and spinning machine parameters, but they did not change the chemistry of the viscose; they used their viscose systems. None of these 18 samples met the requirement of the specs that I gave you earlier. The ones that they have problems with are conditioned break strength, conditioned elongation, and shrinkage. Three of the 18 formulations were selected as essential re-entry vehicle of propulsion in the D5 program. As far as I know, 5500 pounds have been made. The next three charts show what was selected from the 18 are experimental runs 16, 12B and 13A. Chart 4 depicts the spec requirements and Avtex's average values that they produced. On this column, I have the trial or experimental run for 6B. When North American Rayon put it into production, these are the numbers that they got. Elongation does not meet the specs in the 5.5 to 9.5 range. Also, there is a difference between the trial run and the production run; it is not consistent. In shrinkage, 5.4 does not meet the specs. You also have a difference in the prepreg, 5.4 and 5.7 from production and trial run. They have problems with the finish, 1.3 to 1.7. There is a difference in trial and production, also in ph. The 8.7 does not meet the specs, and there is a difference in the 8.7 and the 7.3 final production. North American Rayon has decided not to make this anymore, because they cannot make it consistently. This trial run and the production run is not consistent, so that say that they will not make any more 6B.

- P. Pinoli They have indicated that they do not want to make that product. Before you remove the overhead, Lou Ann, I want to ask a question. With regard to that pH, what went wrong when it varied from 7.3 to 8.7?
- A. Turbak They obviously did not get enough out of that thing. I ca not talk about their conditions. If they were to neutralize the acid ????.
- D. Beckley In reality the 8.7 was a worse situation than the fact that they ended up at 7.3. They actually got the product. (group discussion)
- J. Thomas Lou Ann, how do you pan (inaudible)?
- L. Fikes As far as I know of, the 5500. That was what was pressing.
- J. Thomas Is that enough poundage to determine the variability?
- D. Beckley Jim, they have indicated a capability of about 1000 pounds per day; they probably did not produce it at that rate. This is 5 running days on a machine.

- L. Fikes Of these 6 figures, D5 selected 1 of the 3 that to make runs out of; they still have problems with the others. Trialwise, for the elongation 12.6 is not in a spec. We also have a difference between the trial and the production of 11.2 on elongation. On the shrinkage, 5.4 and 5.6 does not meet the specs; also again they have a problem with the finish of 1.4 and then the difference between the trial and the production of 9.32.
- They are saying that they have the finish figured out now. They thought they had it before, but they are trying to make some more runs to see how close they can come to making a finish like Avtex. This is the third one in which the production 13A across here. The elongation, shrinkage, and finish are all out of spec. The D5 selected 3. One of them is out now because NARC said that they could not make it consistently anymore, so they had to make another selection for that third one. That is all that I can say about that.
- J. Thomas What is the difference between A and B; I assume that 13 is ???? yarn.
- L. Fikes The experiment is 13. There were 18 experiments in total.
- J. Thomas Why A on some and B on some?
- P. Pinoli They worked with slight modifications to a 13-grade material. Their reports indicated that they were similar in nature. In many cases, you would have difficulties discriminating between the two at the rayon level, but we assessed the effect on the carbon fiber.
- D. Beckley Some process parameter let them call it an A or a B or whatever.
- J. Thomas Was there an A and a B on all of them?
- D. Beckley No, just on a certain number of them that came off that way.
- A. Turbak When they could not spin it, they went to slightly different conditions and then called that A and B.
- P. Pinoli North American Rayon has indicated difficulty removing the finish from the material, using their standard technique of extraction. They have asked for some help from this committee, and we were interested in getting involved and proving the test methodology. We reported that it is an open issue, and I think that it is appropriate for this committee to get comments at this time.
- M. Towne How were they measuring it, Pat?

- P. Pinoli They were measuring by the soxhlet method, but with different solvents.
- D. Beckley There are really two accepted, industrially practiced finish removing techniques, using different solvents or different solvent combinations. Their standard methods did not conform to the method that Avtex used, so they switched to the Avtex methods and did not get immediate gratification in terms of results; therefore, it has created a problem in their minds that needs to be worked out.
- P. Pinoli We still have to settle on what type of finish is desirable for rayon.
- L. Fikes They think they know what Avtex has used in the finish, but they are still running tests to make sure. This chart is a summary of the last 3 charts. Figure 7 lists some requirements--strength, elongation, moisture, and DP. The DP of Avtex has 325, whereas, North American has 425; they need to get the shrinkage down, copper number, and core ratios.

On April 10, NASA authorized North American Rayon to proceed with some facility modifications so that North American Rayon could make us a line. The line that they have been using before was for commercial use, so they could do experimental runs for us, then go back and do commercial runs. The reason for this line is so that they can not develop an Avtex clone on a separate line. They could make changes on this line that would not effect what the commercial folks needed. They had 5 weeks to complete these facility modifications which included the finish system, the viscose system, spin bath system, and instrumentation. They also were to put together an experimental design which included 16 runs.

- L. Fikes The five weeks is from April 10 and the 5 weeks is up today. The facility modifications have been completed, and I will discuss their schedule later in my presentation.

The parameters that they can now vary in this experimental design include the viscosity, the caustic content, the cellulose content, and the CS₂ content, but they can not change any of the numbers. Chart 10 depicts the schedule which is to begin May 17. Last week was the end of their fifth week for the facility modifications, so their first experimental run was to begin yesterday, and spinning will actually start tomorrow. Two variations are planned for the first week; three variations for the second week. The plan includes 16 variations, and it will take North American Rayon about 3 days to complete the critical required testing after they have finished 1 experimental run.

I also have a list of additional rayon characterization tests that will be run at Morton-Thiokol and the MSFC M & P Laboratory. These include conditioned tenacity, wet tenacity, wet break strength, wet elongation, conditioned modulus, wet modulus, hemicellulose content, skim to core ratio, copper number and trace metal analysis, sulfate and sulfur content, and S₆₅ solubility. Chart 12 provides a summary of the rayon development and qualification schedule. It begins with these 16 runs; they have already completed 18. They have completed the facility modification, and experimental runs should be completed by the middle of June. Chart 12 also depicts the qualification plan which includes weaving, carbonizing, and prepregging, all the way to the static firings. That is the overall plan; everything depends on what happens during the 16 runs.

- J. Thomas This schedule is a year behind the original schedule that they had. Their qualifiers were supposed to be completed in December or May, and you say that this will be completed in November--16 runs and a year later.
- L. Fikes You have to remember that in the first 18 runs, they tried to use their viscose system and did not go to the Avtex system. Viscosity changes could not be made on their commercial line. On a line dedicated just to NASA, they can make all kinds of modifications and it will not effect their commercial work.
- J. Thomas I think they are determined to put up their share of the funds and I think NASA is going to be inclined to do that. DOD is not going to be inclined to do that because they were not inclined to put up their share of the \$43 million. Whether they can be convinced to come up with another several million per week, I do not know.
- D. Beckley Jim, it seems as though the programs in DOD individually, that could lay back before, are now coming to the front, which need a life-of-type procurement to cover them for 1990, 1991, and so on. Many of the programs are going directly to highland so that they can attempt to utilize that warehousing. Where the funds will come from to cover each of those, is really not clear. I think that as it becomes evident that they want that material then they will realize that the only way that they are going to get it is to keep Avtex going x number of months more. Much depends upon how many programs there are.
- J. Thomas Actually they say that the ??? , so that they can come forward with x number of months more to go do that. Their quantities are . NASA is the only true production and you have to have 24 thousand pounds per week at present now to keep it going. No one else has that; NASA is much more dependent upon Avtex until 1991. I just hope that they realize the need for Avtex, also.

- D. Beckley I think they are beginning to realize it.
- P. Pinoli I think you also need to comment, Don, that all the major DOD programs are very slow to react and put money up front. Are any individual programs in a position to jump very quickly to save the Avtex operations?
- J. Thomas I think that NASA is in a more unique position and has committed to support Avtex knowing in all probability that something ???? to ??? the system (Inaudible). We have to save Avtex. Then they need to go and stick their necks out and commit the agency to that. Frank did the very same thing with Kerr-McGill in ?????. He went out and committed that, and the agency came through and supported him on it. When we find out what the requirements are, then we need to go and get some advance money and we committed to that material to get it into the system. We need to give Avtex more money, because then we get a product in return.
- D. Beckley One of the problems with that thinking Jim, is that a commitment normally through the system does not end up as a payoff of money until the final product is delivered. That does not really give Avtex any money to keep payroll going, but you will have to put it up front. It has to be a totally different financing scenario to solve the problem.
- J. Thomas But if they are losing 4 to 5 million per week from their staple rayon, the 3 billion pounds does not out. There is just not enough money to do that.
- P. Pinoli Tom, you are next up--to change the subject to GPC resin quality control.
- T. Bhe I am going to talk about phenolic resin quality control. Figure 1 shows the carbon-phenolic composites processing diagram. The phenolic resin, fabric, and filler are impregnated to produce prepretape, which is used in the tape wrappint process. After tape-wrapping process is completed, the part is cured and machined to produce carbon/phenolic nozzle. The producibility of quality nozzle depends on the quality of the incoming phenolic resin received by the prepregger prior to starting the impregnation process. More specifically, the degree of advancement of phenolic resin can affect the processing and nozzle quality. From the nozzle fabricator side, when the degree of advancement of the resin in the "as received" prepreg is too high, the tape has no tack to be able to tape wrap the part properly. Thus, the tape has to be stripped off from the mandrel and resulted in higher cost of fabrication. If the loose tape, due to lack of tack, stays on the mandrel, the resulted part will wrinkle after the curing process. The variability of degree of staging of the resin in the prepreg can cause

delamination and compaction problems in the final nozzle hardware.

The current resin acceptance specification used by the prepreggers does not adequately finger print the resin behavior. In addition, the minimum and maximum values of the tests required by the specification are too broad. A typical tests are total solids, viscosity, specific gravity, gel time and stroke cure. The prepreg acceptance specification does not contain tests that can fingerprint the resin adequately. All the tests listed in both the resin and prepreg is "old." IN the last meeting, I presented a "newer" analytical technique called GPC or gel permeation chromatography which can characterize the molecular weight of the resin in the prepreg. Figure 2 shows the increasing molecular weight of SC1008 phenolic resin with increasing time at 110⁰ C or aging. The current resin acceptance specification test values mentioned above are not sensitive enough to pick up the increase of molecular weight due to aging or resin advancement. Figure 3 shows the increase of molecular weight of phenolic resin before and after the impregnation process.

- D. Beckley What is the before and after of that, Tom?
- T. Bhe Before impregnation?
- D. Beckley After impregnation? The real comment, and it is deceptive and difficult to see, is that what you have really done is lose the free phenol peak. It is difficult to tell how much increase you actually have by virtue of losing the bulk of that phenol from it.
- T. Bhe The decrease of phenol peak after impregnation process is due to the further staginf of the resin in the prepreg going through the tower.
- D. Beckley By losing the principal component of this, you think you have a higher molecular weight, but all that you have really done is, literally, the solvent portion (??? the semi-solvent that the free phenol represents). The highest percentage of this one is the free phenol (Fig.). When you remove that you seemingly have incurred advancement, but what you have really done is taken a large amount of the numerical change and shifted the indicated molecular weight.
- T. Bhe No, the molecular weight is determined, using a calibration curve of known molecular weight compounds.
- D. Beckley It is a very small amount, much less than the number 4 to 6 change represents.
- D. Beckley Is it in the resin?

- T. Bhe Figure 3 shows the increase of molecular weight from 411 to 678 after impregnation. Figure 1 is the lot-to-lot variability of the resin molecular weight. Resin I is the 91LD for 2 different lots tested 3 times and Resin II is the SC1008. Ironside uses the refractive index detector, but Borden used the U.V. detector type.
- P. Pinoli Tom, can the GPC fingerprints discriminate the various commercial phenolic resins
- D. Beckley You are on Infrared now ????.
- D. Beckley These are two different tests: the Infrared detector versus Infrared spectrophotometer.
- P. Pinoli That is where I am confused.
- T. Bhe We are talking about ultra violet or U.V. detector in the GPC instrument not in Infrared detector. Infrared spectrometer is a totally different analytical equipment than GPC. In GPC technique we have a choice of which detector we want to use, refractive index or R.I. or U.V.
- P. Pinoli Are you saying that we need standardization?
- L. Fikes Is the instrumentation the same in all places?
- D. Beckley No.
- P. Pinoli Do you think that it is possible to standardize the GPC test, based on your experience?
- T. Bhe Yes, it is possible to standardize the GPC technique.
- D. Beckley I have a memo that our analyst prepared as a result of a question and what you really have is a summation of three sources under consideration, columns, temperature, flow rates, solvents, detector UV versus RI, injection volumes in microliters, sample concentrations, sample size, standards being used, integration limits, and effectively what happened--2000, 3000, 5 to 6 and 3 to 4. We are all running the same thing and we have totally different pictures of what is coming out. This was prepared in 1988. We looked at our data from 1983-86, and from 1988 and 1989, our data is tending to go over to here (Fig.). We are getting very low numbers and as the data user, I don't know why. I have a feeling that it is in the procedures. We are bringing resin in time after time; we have many other parameters to talk about the behavior of the resin. We do not see any changes as manifold as that, so I honestly think that we have a procedure (internal) problem. We did one other thing. You had the series, Tom, of the one week; we did a week at 90°F and in some testing, Infrared in particular, we would have a

marked change in the resin. Our GPC data did not change in a week, and I do not really understand that. It seems like the state of the art of what I am reading is not comparable. Tom has made more progress with it, conceivably more than anyone else, but I am not sure where we ought to head.

L. Fikes On that chart that you just had, (Fig.) do you have two different ways that the sample is being prepared, ?

D. Beckley Yes. This mainly summarizes the assessment of it. Sample concentration should be in this interpretation (dilute, instead of heavy), and that is probably the major difference why Tom's numbers are up in this range where the other numbers are in the low range. The implication is that if you overdrive the column, you are liable to get a different interpretation. Even the standards are a problem in that we talk about polystyrene standards and give them a 35,000 standards. It turns out that they have a number average of something like 25,000, and they are not controlled from place to place. There really is not a NBS standard to use. I do not think that that is the discriminator in this instance. We have bigger problems than that. The standards are not working very well for us.

We had some experience using ultrasonic to get the specimen off, and this is probably one of the biggest problems in the whole analysis. If you use an ultrasonic device to get the resin off the fiber, you have actually changed the resin; it has torn the resin apart so you end up looking at a different polymer than you would have had you not used it. So, cut and dry degradation is just not going to work. In view of the fact that we run hundreds of soxhlet extractions per week, and we know that there is a percentage of resin that is left behind I have some difficulty wondering if this technique is really telling us what we need to know in the late B stage.

L. Fikes What size sample are you using? Is it the prepreg itself?

D. Beckley It is projected that we can use this analysis to check A-stage resin coming in; that is in the solvent and so on or we can use it to check prepregs. When you get into the prepreg, you have to extract it off and we are not certain how we extract it off to get what we really want to see.

P. Pinoli Tom, what technique are you using?

T. Bhe The extraction takes 24 hours, overnight in solvent THF.

D. Beckley Here is a comment on THF. [No sample the H and THF, which is a notorious peroxide, former THF makes peroxides,???) and the peroxide attacks the phenolics so if [you??] are in there for a long enough time, the THF is killing you, in terms of having the same ???? .

- T. Bhe The THF used in testing the molecular weight of the polymer is generally HPLC grade, which contains minimum amounts of peroxide.
- P. Pinoli Tom, you said that you used 24 hours; do you use agitation at all?
- T. Bhe We do not agitate the ample in the solution.
- E. Hemmelman I have a problem with that ?????. I do not know if I can afford to wait 24 hours after I have made the product.
- D. Beckley What he is citing is the fact that to run this test as we understand it, takes 1 to 2 days to get the standards ready to go, and then about a day to get 1 to 2 analyses out. It is not a practical end process quality control tool (group discussion about prepreg and real process data). It takes too long to get it, and is really too expensive. Three man days to get a data point is not very effective.
- T. Bhe This probably could be optimized later when every resin supplier and prepregger agrees to use GPC for Q.C. Now from our end, we have prepreg that meets all parameters in the spec, resin solid, flow resin, and volatile content. When we try to tape wrap, the tape does not stick on the mandrel; you end up stripping it off and throwing it on the floor.
- E. Hemmelman I agree that there is something that we could do to eliminate that problem, but I am not so sure that this is it. Maybe something else needs to be done. Obviously all the prepreg manufacturers are interested in making material that tape wraps 100 percent of the time, and not just making materials that meet specifications.
- P. Pinoli Tom, do you feel that the GPC test that is used to discriminate resin molecular weight can be used to assess if a pre-preg tape can be wrapped?
- T. Bhe From our experience, we have to look at it (the problem of the tape wrapping process). We get better control of the wrapping.
- D. Beckley Tom, if you will let me share with you, I would like to try and address Pat's question another way. This is another kind of molecular weight determination using electrochromatograms. We use the same equipment but in a different way. This is the same phenolic spectrum that is crammed together as one peak and then a broad band. This is not separating the bands out into what turns out to be individual constituents, or at least some more different constituents. This peak in Figure is the standard peak. Here is the phenol standard and here is the curve standard peak that is superimposed on here. This is giving you the

ability to get a controlled amount of these peaks. You compare this peak to this one, and you compare this peak to this one, and so on; you can get controlled amounts. Furthermore, peaks 1 and 3 are directly relatable to the 2 peaks used in the infrared analysis (a quantitative type analysis). So the end result is that this test is a 3-day test, too. It is another way of looking at the analysis. People who have gone into depth like to talk about these being monomeric species. As they are polymerized, they become dimer species, and the dimers become trimers, and the trimers become quatramers, and you build up the viscosity. If the prepregger has a molecular weight of 190 coming in and has some of [these??], and then he gets a molecular weight of 187, his end point is still somewhere down the road. We probably make up for small differences in molecular weights on incoming resins by the A-staging process. I am not sure it is really critical that the A-stage resin be one fixed number or within a band because a process indicates that we need to advance whatever we have to a different set of end points and ?????.

Figure is an attempt to look at what, I think, one of the things that the prepregger does. He takes a given material, in this case, carbon phenolic materials and questions how to fabricate material? There are, 5 or 6 different techniques and material. We tailor base upon the cure pressure for those things and we speak to each other in languages of "make me a volatile range here, here, and here." You can see the descending order of all range that is used to define a given product; likewise, when you find this one, you ask at what flow pressure do you want to define it. Figure shows a band of similar flows at different pressures, which is really a viscosity measurement of the summation of things. It assumes that the resin content is set in at the agreed upon level. Each of our customers likes to have a slightly different resin level for the same product, so you have to set the resin level. Then you come along and talk about test temperatures, which is a wrapability issue. You can talk about the product in terms of IRZB, and this is a test that also shows a nice continuity with the tailoring of the material. This one is operator dependent to get an end point that is a cloudy or hazy point. You really have to be reading it. I want to understand if there is a need for 1, 2, or 3 more tests to find what is the continuity of this. If so, we need to run them, literally, on every roll or every part of it to be of use. We can take a spec, an order, on any one of those things and add a couple more tests, but we really have to be able to run the tests in a real time if they are going to be of any use.

T. Bhe

I do not think the test is any different than we have been having for the last 20 years.

- D. Beckley Tom, that one is brought about by what has turned out to be a unique thing in industry. We have people using an autoclave to cure ????? grade materials, so it has extended the range for the autoclave fabrication. This is some of the range that is used, but on any given run, it is not going to be that wide. For any given customer, it will not be that wide. When you have someone taking ??? grade material in, which is really more coarse pattern grade, and then curing it in an autoclave, this is what happens to it; therefore, you need to extend that range. It is complex. This is the same foil running 150 or running at 1000 and the differential is a 10 percent number.
- D. Beckley The material will get into your system.
- T. Bhe I could mix the resin of high advancement which will create low flow and low advancement which will create high flow. When the 2 resins are mixed together, they will make the prepreg and satisfy the resin flow spec requirement, but it does not guarantee that the prepreg can be tape-wrapped with sufficient tack. We have seen it over and over.
- C. Heinze First of all, tack and molecular weight are not directly proportional. Also, the degree, molecular weight distribution, has a lot to do with this. It is not just where the molecular weight is, it is how it is distributed.
- D. Beckley If you have heavies and lights, you have an average that is here, but you have an entirely different product.
- C. Heinze In mixing, you may or may not have tack, and you may or may not be able to change that. Secondly, when you do GPC on a prepreg, I think that you are not getting the real number that you want. You are not getting a viscosity profile of the prepreg introduction. Once you start advancing resins that you put in, you are not getting a resin evaluation of polymerization. The molecular weight distribution will change the tack.
- D. Beckley They do not even go very far. Quatramer is probably the upper end of the molecular weight of the phenolics that we use. The next thing that happens in the cure process is that you move into the cross link mechanism and the molecular weight ceases. You have locked it at that point. We do not have a polymer that has a neat way of evaluating it from molecular weight standpoint because we do not have a wide molecular weight range. We are not building long chain polymers like thermoplastics that have molecular weights of 2 million or 100 thousand, or anything like that. We are just barely in the low thousands of molecular weights at the cure point. So, it is not an ideal test for molecular weight measurement; we are squeezed into a very narrow area.

- T. Bhe We also look at the dynamic viscosity of the prepreg, using rheometrics mechanical spectrometer or RMS.
- C. Heinze That is where you are getting into the scientific approach of it (the dynamic mechanical thermo-analysis of the prepreg) which is tricky. You have to recalibrate the instrument, (the reometrics type instrumentation), to cross-correlate, so the GPC is very evaluation. Then when you get it to prepreg ???
- D. Beckley I am really on the fence whether it is worth the effort to get to a standardized method that everybody can live with.
- C. Heinze Is there a reometrics test on a prepreg that you would use?
- T. Bhe Yes, we have been running dynamic viscosity on the prepreg. It will tell us if the resin is too green or too far stage, but the RMS is expensive, and not every body has it.
- P. Pinoli Tom, do you propose to use the GPC to evaluate pre-preg material, as an acceptance test?
- D. Beckley The use of GPC from 1983 to present, is that we have an activity we call fingerprinting. We have 80 or 90 tests that check the resin before the resin meg is checked with the filler, the fabric. As part of every test that we could think of, we run (group discussion),???. Our history is that we were running up in this 2000 range, but all of a sudden for no explainable reason that I can find, we are now looking at 400 and 500. I have a feeling, knowing what the resin is doing across the board, that it is not a resin change. In fact, both suppliers, say that the molecular weight is down. Ironside says that the molecular weight is down, and our test data verifies that. But nothing else of the specs that we checked the resin indicated change. I think we have an internal drift.. I have no idea what it is, ??? procedures.
- B. Hall Let us take a 5 minute break.
- P. Pinoli The issues on the table now is carbon assay accuracy and test procedures with regards to equipment currently employed by Hitco, Polycarbon, and Amoco. We want to know how to assess the accuracy. Gene, do you calibrate your equipment to a known standard?
- G. Rubin No. We push a button. In the sense that you weigh the sample on a calibrated balance and you weigh the ??? absorption of what you have done on a calibrated balance, there is no standard that you normally have to use to ???.
- P. Pinoli Is the machine actually measuring the CO₂?
- G. Rubin Yes. It runs through a cycle where you heat it in a graphite quartz enclosed crucible in an induction furnace,

oxygen flowing through a dust (sulfur) trap, a furnace which changes NACO_2 , goes on and is picked up on ?????? absorption bulb. It is a direct relationship. It is filled with ascarite.

P. Pinoli What is the device you use at Hitco?

G. Rubin The device is a retrocarbon analyzer, model 521.

P. Pinoli Miles, what are you guys using at Fostoria?

M. Towne We use something that is very similar--the ASTM D3178 system that uses the triple absorbers, a Nesbitt bulb, and Ascarite II; for this we do not feel that we need a calibration. It provides us the amount of carbon graphite. I do have some data on the reproducibility and also on the comparison with the other Leco model that measures carbon, nitrogen, and hydrogen together.

Group discussion

We looked at all 3 of the Amoco products and this is the NEC (the name of the operation at Fostoria--National Electric Carbon). They are also one of the tenets at Parma, so we do a similar procedure at Parma. When I have carbon analyses that I want to feel more confident in, I go to Fostoria to get the carbon analyses that I need. I have a high degree of confidence in the data that I get. Again, it is the Ascarite II. We do not use the lead chromate in there, and we dry the sample (0.10 to 0.15) for 30 minutes at 110°C before we measure it. This method is for analysis of coke and coal, so the procedure describes how it is milled. But if we use it, we use a small sample of cloth.

T. Bhe The same size and the same procedure?

M. Towne Yes. Figure 10 denotes test results that (looking at the VCK product) are the kind of reproducibility that we get is a very good standard deviation. We looked at VCL, which of course, our product is lower carbon; this was a sample that we looked at from these three. This sample will also be used in the LECO system, and this is our average. WCA, two different samples were hanging just a bit above and below 100, the closest we measure.

P. Pinoli Three significant figures seem to be generally reported.

M. Towne Yes, I think so.

P. Pinoli What is your sample size in milligrams?

M. Towne 100 mg (group discussion)

D. Beckley Tom, did you have anything to add?

- T. Parai Basically, it is the same thing.
- T. Parai You questioned standards. We use a LECO standard for the alloys; there are two methods that we use we prefer the LECO Cr12 (an Infrared CO2 analyzer). The question about sample had come up, and just for sake of kicking it around.???.
- D. Beckley You could wait until we are done here.
- M. Towne I do not know the number of this LECO, which is one of the major 3 constituents (Fig. 11). We do not have this, but we do have a pretty good study run comparing the two. We wanted to see how close it came to getting the results that we got. These are LECO operator results; these are not our own operator results.
- D. Beckley Miles, in one way, that equipment is so automatic that when you load it, it does everything, including your answer, without touching it. I am not sure what the operator does with this equipment (the CHN600).
- M. Towne I do not have one.
- D. Beckley That is using the other side of the house.
- P. Pinoli Don, does it automatically predry the sample?
- D. Beckley We have been using one for about 2 to 3 years, and for us, we were one step back from where Miles' work is in terms of technology. It made a manifold improvement in our accuracy of results and reproducibility to the extent that I do not think there was a problem.
- G. Rubin I am not sure that I buy the accurate, repeatability, maybe.
- D. Beckley Gene, we do the same thing. We run a standard on it that is basically 100, and the answer comes out 100.
- G. Rubin I understand that, but I also know that with that particular filler unit, they have had tons of problems with it.
- M. Towne When they started these runs, they tried to standardize the unit, and this was one of the materials that they tried to standardize. I guess they also tried to standardize the sugars. Then when they ran the carbons, the results were quite high. When they tried to standardize with sugar, it was not even in the ballpark. However, then they used WCA as 100 percent standard and from there they ran the same sample 10 times that I showed you before called VCL. This was the number they got; standard deviation is good, and this is the range in values within minutes. Then they ran the WCA again and got one high number here (100.03). Three

standardized on the basis of this again to 100 percent. They then ran 10 for the same VCL again and got a number a little bit lower, but still pretty close in the range of about the same. They ran the WCA again and were up again. So, their concern was that maybe the operator had a little problem, but they thought the frequent standardization with WCA was necessary. This, in the course of a day, can be run several times to make sure that the units are standard. These are the results of the LECO people.

It looks like it is certainly possible to get the same kinds of results.

- P. Pinoli I think what we are concerned with is test accuracy. On that basis, Miles, if you report out a 99 percent material, what would be the low value and the upper value that that material would probably not be judged beyond? If you report a 98 percent, would you say that that material is between 97.5 and 98.5 percent?
- M. Towne The higher you go, the closer you are going to be as long as you keep the standardization up.
- P. Pinoli Is the LECO device that you are talking about a vacuum device or is it positive pressure flow?
- M. Towne I do not know.
- D. Beckley I do not remember the details on it, but it is automatic dry.
- P. Pinoli What scares me about automatic dry is that you can get into oxygen chem adsorption. The longer that you hold this activated carbon at any moderate temperature with oxygen present, chem adsorption will occur, adding oxygen to the carbon surface. That will change your carbon assay number because your initial weight will turn out to be higher. How much change you get with 30 minutes drying, I do not know. I was more concerned about how you treat the moisture content with respect to carbon assay.
- G. Rubin Yes. That would have to be the low carbon assay number.
- P. Pinoli All three of the carbonizers are drying your materials.
- T. Paral We had some of our people chase down some information on standards--how LECO does their standards and how we do ours and how the National Bureau of Standards handles their information. Then we wanted to know how it ends up being an NBS traceable standard. It is quite interesting to see how they arrive at their number for a National Bureau of Standard traceable code. These are code standards that they provide for us. Basically, I think that if we look back and compare everything, then we are right down the line with about the same thing. Only about 1/2 percent is what we

usually look at, also. We do use a CR12, basically a similar machine like Don was talking about except his would be ??? and hydrogen at the same time. Ours will not do that; it is strictly a carbon analyzer.

- P. Pinoli I think that our current feeling on this, Bill, is that we should send out round robin samples and assess the testing results.
- M. Towne What samples were you going to send out?
- P. Pinoli We will send each of you some similar predesignate samples.
- M. Towne With some variation in carbon.
- P. Pinoli Maybe 3 of them. We will try to keep it to a minimum and a standard to see how you all compare. We will then sit back and look at the numbers to see how closely the numbers match. If they look close enough, I would say that we are in pretty good shape. Anybody who wants to have a strong feel for test accuracy and laboratory variance can review the numbers.
- M. Towne I think that you should use a few samples and a few runs, not just maybe send 3 or 4 samples. Anyway, You should, at least, use 5 or 10 of each of those samples.
- P. Pinoli I think that I will talk to each one of you individually during the course of the next few months, and we will set up something that we feel comfortable with.
- Lou Ann, would you volunteer to participate in the round-robin?
- L. Fikes You could talk to Pat Johnson in the chemistry department; she has the equipment there.
- M. Towne What kind of equipment is she using?
- L. Fikes I do not know. That is a different branch than I am in, but I do know that she has carbon assay equipment there.
- P. Pinoli We have an agenda item next on ultrasonic testing; I think that this is covering some old ground.
- D. Beckley It may be old ground to you but it was new to us. There is a company known as Test Incorporated out of San Diego, and they are beginning to market an ultrasonic analyzer that can measure resin content by their indication and they can measure it as a cured laminate. They can supposedly measure a cured part, assuming that they can get the shape to fit the analyzer, and they are having some degree of success measuring prepreg. We took an interest in the area of measuring prepreg and for the principal reason, the

analysis itself takes essentially a few minutes to do. If you have as many analyses to make as a prepregger does, you look at roughly (inaudible) situation you need in process control. You need a certification test method, and then you need to be able to confirm the resin content of a laminate. In our situation, these are the assessments, economically, as we are talking about a \$100, 000 piece of equipment. Our assessment is we do not do enough platanol resin content to make it of dire interest to us, At least there is some interest there, but we have to do at least the end of every prepreg roll, sometimes the starting end. If you add up that number of rolls per year, it becomes somewhere between 5 and 10 thousand rolls. If the cost per test (a soxhlet extraction or something like that) is in the vicinity of \$20 to \$25 per test, (man hours time), and you add this test that can do 5 or 10 thousand per year per minute each, just the labor cost alone makes the unit attractive. So, we polled and decide to find out about it. Figure indicates the curve they produced. The curve compares acid digestion costs in terms per pounds of test per year which illustrates the \$20 test (typical versus where they think they could get into a \$5 range), and that is amortizing the equipment plus labor costs, and the piece of equipment looks something like this (Fig.). An operator stands beside the console and all the important things happen right in here. You have a fairly small sample (a 3mm circle), and effectively (tape ended)

Difference in sonic velocity or ultrasonic velocity through the resin phase is different through the fiber phase. In our case, it is different than the velocity through the filler phase. If you have a fixed velocity for each of those components, then the composite velocity becomes a number. I have spread it across the resin range and expected prepreg. This is assuming some differences in velocity, enough to give you a calibration. That is the key. They believe that once the product is calibrated, with the calibration curve, that puts known samples on a line and compares the ultrasonic velocity. You can then come back and at any time get this equivalent velocity which is that resin content.

It all sounds good until you start to consider a couple of the realities that are not pinned down yet. Figure depicts a description of the techniques of a series of laminates of different resins contents, the method of measurement schematically described, basically then developing samples with given resin contents, and a calibration curve comes off of that relating these resin contents to measure velocities. In prepreg which is of interest to us, we have a fourth phase which is air for void content, which also has the sonic velocity. It is such a significant difference that in our initial experiments where we were measuring it, we were not getting reproducible results. It soon became evident that we had to get the void content out of it. Now, you are dealing with the fact that you would like to make a no-flow

laminate that is void free. That is really going to become the next step in the name of the game. They have learned in their work that because of the small sample size (roughly less than 1 inch in diameter) they want to stack together 7 or 8 layers; therefore, they are going to make a 7 or 8 layer laminate, taking out sections, putting them together, putting them under controlled pressure, making a void-free structure, and sticking that material in the analyzer and getting (inaudible). If we can achieve those things, then we are down into the 1 minute analysis time and progress will have been made. The group themselves are in contact with ASTM and hopes to come out of it with an ASTM number in a short period of time. The technique appears as though it has applicability where the system is simpler, namely an aircraft grade. A high modulus graphite prepreg with an epoxy resin that is soft enough that the void content easily disappears may become a very viable material, and certainly a good reason for it. We are looking at how we can make that same thing work in the ablative world where our materials are basically twice as thick as their cured ply thickness. We have to get that void content out of that. If we can learn how to make the specimen, and if we can find that with the sonic velocity through a fiber it is a constant, it will certainly help in making valid their claim that we only need 1 calibration curve. We spent the day talking about carbonization of materials, and would have to wonder how constant ??? our velocity is.

The second point is that we may find that the calibration curve for assured laminate is different from the calibration curve for prepreg. If this work progresses, you will get a report that says that we can put the "good housekeeping seal on it."

- P. Pinoli Don, I think the panels would be the first place to assess this technique and if it works there, then try and utilize it on pre-preg.
- D. Beckley If you put water as a coupling agent on it to couple the ultrasonic horn into the material, certainly on the panel, it is okay. But then you begin talking about panel surface finish that really should be very good. You are not likely to have a highly variable, normal machine (group discussion about using normal water as a coupling agent). That is the standard, and it makes you a little nervous about any reading that happens after the first few seconds because you are dealing with a water diffusion mechanism that is going on.
- P. Pinoli What effect does crenulation lobe voids in filaments have to do with test results--old Avtex versus new Avtex? Will it respond differently?

- D. Beckley If we had a void-free structure (resin taking care of all the places), it does not matter.
- P. Pinoli In the composite you have the void in the filaments. All of my microstructure data shows that a large percentage of this void never gets resin in them.
- D. Beckley The danger there is that may become a slight factor that is unavoidable.
- G. Rubin Would not a standard take care of that?
- D. Beckley If you calibrated out and it is a constant, then that is okay. But the day that we go from viiiwite with no voids to new North American that has 50 percent voids, then we have a different standard. It is all 49/26.
- P. Pinoli Don, do you have special internal funding on this assessment?
- D. Beckley No. The company is desirous of a way to reduce quality control costs, and we have to say that it will certainly have to be independent upon this group to turn in a recommendation to be incorporated in lieu of the resin content method we have. We are coming to you up front saying, "If you encourage us to go ahead with this, we are going to build ourselves an obligation to push it along instead of I ca not make a change because it is different." We would like for you to be aware of it and why we are looking at it.
- P. Pinoli Ed, are you guys looking at the same device?
- E. Hemmelman We all want our ????.
- R. Yost In our Measurements and Effects technology group we are doing some work on that; I have not touched base with them recently to find out exactly where they are and how close it is to becoming a Quality Control test.
- D. Beckley It has a good report at Morton-Thiokol on a set of glass phenolic panels where you can run a burn off immediately after and see the results.
- R. Yost We have worked a phenolic prepreg, also, on glass carbon reinforcement. I have not seen the results of that yet; we are investigating all the major resin and reinforcement combinations.
- T. Bhe Is the resin content value obtained by ultrasonic method an absolute value.
- D. Beckley Basically you have an ultrasonic number, resin contents, and a standard number. You put your specimen in it and because

It is all computer controlled, it measures this value, runs across here, and says that this is the resin content (Fig.).

- T. Bhe It is similar to GPC technique where the standard curve of known molecular weight compound need to be generated prior to testing the molecular weight of the phenolic resin.
- M. Towne Rob, do you have a set of standards for each of the fibers that you use
- R. Yost We do during the calibration process--acid digestion versus what the instrument measures. We measure the sample on the instrument and then perform the digestion to find out the value of the resin content.
- D. Beckley If you change from T300 AS4, do you need a new standard? (No verbal answer). Okay, that is a clue for what?????. If you looked at T300 last week , do you know? (group discussion)
- T. Bhe Can you separate out the filler content?
- R. Yost We have not tried it on ablative type materials. We have stayed within the safe area--graphite epoxy which is not filled. We have not tried to measure the filled resin systems yet.
- P. Pinoli It is nice to have a piece of equipment that is being used effectively in another area so that you can watch it build up your data base and confidence on a simpler system.
- D. Beckley This is defensive because we know that pressure is building and left to their own device, this company will publish to the world that it has a cut and dried answer. We need to know if it has an answer or not, so that is part of our reasons for doing it. We do not want to get a pig in a poke shoved on us, if it is not going to work. If it is, there is ample reason for it, but on the other hand, we have tried to say today the things that are apparent as potential problems about the systems.
- P. Pinoli You are right about one thing, Don, about the tremendous cost impact. Bill, I think you were going to give us a little bit of a rundown where NASA is on the issue of cured CCP acceptance testing.
- B. Hall As I mentioned the first thing this morning, this is 3.2 part of the SPIP program. As Dick Herman said, there is a 3.1 counterpart which is concerned with test methods, and specifications for the curing parts. They had a two-day, initial meeting at Marshall a couple of weeks ago. There were 3 companies there--SoRI, ARC, and FMI. They introduced

the tests that they run, telling about the specs they use, nothing more than definition.

There was a gentleman at the meeting who was in charge of the Mill Handbook 17, and he said that the way you establish a handbook, is that you appoint a committee that meets twice a year at interesting places so that people will keep coming back. This is our third meeting, and we have a committee that meets twice a year at interesting places, and this fall we will meet at Tempe, Arizona at Fiberite. Next spring we will meet in ??? California. Then we have an invitation for the next one, so I think that we are following the guy's recommendations. Of course, the final end product of this meeting will be updating the handbook that was published a year or so ago which is right now a compilation of the tests that we obtain along with the entry sources. We are well on our way. Are there any questions about the meeting at Marshall?

D. Beckley

I would like to add that Bill and I sat there, hoping at the meeting we would hear of a replacement for the shear test that is currently running in our industry, namely the double shear test 41A type. As the day wore on and all the specialists in the 31 testing, made presentations we concluded that even though our test is no good, they concluded that there is no other test that is any better. Every test that mankind has perceived has a component that is either tensile or compressive in side loading to the test. Therefore, it is not a pure shear. Now, I personally am not such a purist that I would let that stop me, but the overall situation is that they did not have enough good to say for any of these other shear test. They considered about four of them that I feel that we could have brought to this group and say "we want a change, as bad as the test that we have." As sensitive as the test is to the tooling, the laminate preparation, all of the factors that go ahead and make up the number, and as we go into pan with lower shear numbers, it is going to become more critical because we are going to be bumping against the bottom limit that designers do not want to go under.

P. Pinoli

Did you get the feeling that that particular activity was directed primarily to developing test data for the model, not so much the needs of the acceptance test community.

D. Beckley

They want the model to work; therefore, they have to have a shear number that as designers they can live with.

P. Pinoli

I found a total lack of interest in improving acceptance test; the consensus was that there is no good acceptance test being performed, i.e., all mechanical acceptance test data is worthless from the standpoint of the model code needs.

- D. Beckley Try another way that there is distinction between analytical design data and acceptance data that is accepted in their part of the industry.
- D. Clemons Is that test method that obsolete; has it not been obsoleted by the test standards?
- D. Beckley It is still FTSM4 1A in the book as such. The shuttle has taken the method, modified it, and it is in the shuttle spec retinue and cast in concrete for all practical purposes.
- G. Rubin I think that 10401A is out.
- D. Clemons Yes. It is been replaced by an inappropriate ASTM shear. What we have done on our specs is replace it with a double notch, as you know, but we still have some feeling for the pin shear as an acceptance...not as a shear number that you put in the model, but as long as you do the test repeatedly carefully....
- D. Beckley It has worked well to control that product, to limit it. One of the differences is that the ??? fixture for that test is different than the NASA fixture. That fixture is locked at the bottom and does not spread, whereas, the NASA fixture is open at the bottom. You put load on it, the fixture bends a little bit, and you can hear the sample break right in the middle before you get to the two shear planes on either side of it. We have ample reason to be uncomfortable with the test as it is defined for this group, but there is no obvious way to jump into it. Really improved Romanian shear, opescue shear, single lap notch, double latch: they have looked at them and are not buying any of them as a useful number.
- B. Hall Frank Wyler from Lockheed is keeping an eye on this. He knows we have an interest in this and is the contact to keep us abreast of what is going on in 3.1.
- T. Bhe Overall, the meeting on 3.1 chaired by Frank is a pretty good meeting. This is the first time that the 3 test laboratories, i.e., SoRI, ARC, and FMI, have been able to comment on actually what the others are doing. For example, in high temperature tensile testing of cured carbon phenolic composites, each lab has its own standard of specimen geometries.
- B. Hall They are all in different sizes, shapes, and radii.
- T. Bhe I might add that considerable time was spent on discussing the shear testing method. The existing shear test methods do not give us a pure shear strength of the composite. I believe that instead of spending time in coming up with test procedures that will give 100% pure shear, it is better off from the designer's point of view to find out what are the

stresses the nozzle experiencing during flight? Does pure shear stress act on the nozzle?

P. Pinoli I question if an acceptance must provide a pure assessment, such as shear strength, but can provide a combination, i.e., shear/tensile. Acceptance tests must reflect other considerations: simplicity, cost, relevancy, etc.

T.Bhe [3 volume, amorphous.]

P. Pinoli Eric.

E. Stokes We have been working on a procedure to measure the fiber, filler, and the resin content of fully cured carbon phenolic composites. I would like to acknowledge all the people who helped with this effort--Holliis Hill did most of the laboratory work; John Koenig helped with technical support and Clay Clinton gave us financial support.

We did a literature survey and found that there were essentially 6 techniques for measuring the resin content polymeric based composites which are listed here (Table 1). Essentially, this is an acid digestion with hydrogen peroxide that has been hydrolyzed, this is also an oxidation procedure where the materials were fired, and temperatures of nitric acid digestion are an acid procedure. Moisture release combustion is measured on the moisture produced when oxidation of the material occurs. The last one was a hypothetical procedure that was given to us, never tested but just thought up. Some of the drawbacks that we were able to determine from the literature were that the sulfuric acid hydrogen peroxide digestion was in danger of exploding when we added the hydrogen peroxide to the fuming sulfuric acid solution. We used it at the Institute for a while and just could not get sufficient results from it. We discarded it. In the oxidation procedure, you do get lots of graphite. You have to determine, the K factor, which is used to bring back the graphite that is lost. That factor has to be determined on every different material that you use. I should add that the digestive procedure that has been reported but has not worked on our resin systems on combustion. This varies with the degree of composition and the degree of cure on the resin. We tried the last procedure and did not get any digestion at all, so we went on to what we thought was our best chance--nitric acid digestion procedure. It entails putting about 100 ml of nitric acid, a thermometer, and a fork in a three necked glass to your specimen. Then there is a condenser to circulate the cold water to condense out most of the nitric acid. You also have a stir ball with a magnetic stirrer, a plastic heating mantle, and a power control temperature. We tried a number of different specimens and finally settled on this one here (Fig. 2). We wanted to maximize the fiber length and, at the same time, minimize the cost of the

thickness because when these things digest, the cost ply path is the most critical for digestion.

I would like to go through a flow chart of our procedure (Fig.3). We began with 100 milliliters of concentrated nitric acid, heated it to the temperature, and dropped our specimen into the nitric acid. At the appropriate time that the solution is quenched, all the solution and the specimen have filtered through a glass type filter which has been preweighed and predried. Then the filter is rinsed with water and acetone, which helps in the drying process. The filter is dried and weighed and goes through either one of two procedures: (1) a sedimentation process, or (2) a segregation process. Both processes seem to work equally well, but the segregation process is a much faster process.

These temperatures in Figure 4 should be 325°C instead of 350°C . The 4 preceding graphs have that mistake. These are acid temperatures and this is their digestion time. These numbers represent the amount of solid left on the filter as a percent of the initial weight. We plotted all these data points and decided what was an acceptable range for the fiber content (Fig. 4). The range can also be determined by taking a particular acid temperature and looking at the weight remaining. The curve comes down and levels off at the fiber content. This is essentially what we did. We do this to consider the acceptance range for the fiber content of the composite, $51\frac{1}{2}$ percent \pm 2 percent. Then we took some samples, dried them, and did the same thing to them. Figure 5 denotes that the acceptance region is much smaller. Finally, we took some specimens and filtrated them in 1200°C still water and then ran them, and the curve widens out. This is an overlay to the 3 preceding graphs (Fig. 6) showing the acceptance region. Important here is that just around 70 hours, all 3 conditions come together in the regions. What this is telling us is that we are getting some sort of fiber digestion, and the breakup is going through the filter or actual solution of the fibers themselves. The reason that you see differences here (Fig. 7) may be due to the diffusion rate. The diffusion rate is different. Whenever there is moisture in a phenolic resin, the resin is open to more attack. Again, the temperatures should be 325°C . Figure 8 denotes a version of the CCA3 material that we have taken from ASTM at around $2000\times$, and then this is some material that was digested at 48 hours at 65°C .

This one was digested for 72 hours (Fig. 9); again we have 100% fiber recovered. This is one that was incubated for 23 hours at 90°C , and it is evident where the fibers are starting to become pitted (Fig. 9).

T. Bhe

Are those two fibers on the front?

- E. Stokes Yes. For a longer period of time at 90°C, the fibers start to pit and break up. At higher temperatures, apparently some sort of repolymerization of the phenolic resin is going on.
- D. Beckley Eric, do you mean repolymerization of the carbon fiber? Is the phenolic gone at this point or separated from it?
- E. Stokes It happens during the digestion process.
- D. Beckley So you are saying that it refluxes back on it or it is in contact with this phenolic and it ends up....
- E. Stokes It may just be in the suspended solution. Then when you filter it through, it just comes.... This is the filter itself.
- B. Hall Does it all stay together during the digestion period?
- E. Stokes It is sort of a viscous; the color of the digestion fluid changes (group)
- D. Beckley The digestion period, the resin, the fiber, and filler are all together. That is why this comes out looking this way.
- E. Stokes There was a clear, visible difference in the fiber temperatures and times. We did not quite see that with the filler, but this is some virgin Fiberite 7068. All of these composites have been digested at 5055, so the filler is USP28. We did not have USP28 at the time, so we wanted to be sure that the controlled experiments were done with similar materials. We took some pictures of the 7068 and some of the digested USP28 and it looks pretty similar in size and, no doubt, in the chemical composition. Again, Don, we know that there is fiber damage, but we cannot see anything but filler, and we get this coating again (Figs. 10 & 11).
- T. Bhe Maybe your filler is still stable at 800°C.
- E. Stokes We completed all the fiber work first because we did not want to spend all that time working with the filler until we were sure that we had a procedure that would get the fiber out. We have only done a few experiments where we have actually determined both fiber and filler content, and this is the kind of variability that we are seeing. This just shows you whether or not we used centrifugation for the filler content (Fig. 12). These are the digestive temperatures (Fig. 12) and digestion times, and the conditions specifically when we started.
- D. Beckley The resin number is in the sum of those plus the resin equals 100.

E. Stokes One thing that you have to be very careful of here is that these are all determined on "as received" specimens which have about 4.28 percent water.

P. Pinoli Are you running any controls using filler as opposed to the acid?

E. Stokes Thus far, these are the 3 control experiments that we have run (Fig. 13), and we are still doing this work right now. These are approximately the same weight amounts of fiber and filler that we were getting with the digestive composite. That is 1/2 micron in diameter upon the vessel, so maybe we are losing some.

P. Pinoli Is there a chance that there is something else in that filler that you are losing due to the extraction process?

D. Beckley I understand that 7068 filler, so I should not comment; that is, I think, Fiberite's filler.

P. Pinoli Is there any other constituent in that filler besides carbon? Do you expect to see a certain degree of organics.

E. Hemmelman I have a record of what our normal carbon assays are. As to what is in there, beyond the ash carbon content, I carbon assay type filler or 6%....

P. Pinoli My point here is that if you have an organic constitute that goes through the carbon analyzer, some of that organic will show up in carbon. Your carbon assay number will be relatively low. The only reason why you are getting such a low recovery when you go to your leaching process could be the fact that you have pulled out some organic constituents. Am I interpreting that correctly, Eric?

E. Stokes You could be.

E. Hemmelman I cannot really comment because I really do not know. We have never had much success using this type of technique using carbon resins. We used it a couple of times, years ago, and came up with.... We did not carry it through as well (inaudible--someone dropped something to distort sound). We hold it any particular temperature.

D. Beckley It is very time consuming and messy.

E. Hemmelman It also ate up the fibers (group discussion).

P. Pinoli I have to ask an embarrassing question. Why, are you running these acid extractions. Is it for informational purposes or with the intent that you thought they would be applicable to the program?

- E. Stokes To this program I am not sure what the needs are. I know that we at SoRI have a need to know the resin content in order to correlate it with the mechanical thermal temperatures. Apparently, NASA needs to know, also.
- P. Pinoli We do have that need at the NASA program, but there is a test for measuring resin content.
- D. Beckley They use the K factor and a partial analysis (group discussion). I was not sure if that is what your reference was in this oxidation at 390 to 420°C K factor. I think that is referring to that test method.
- M. Towne No, they go much higher than that.
- D. Beckley What is 420°C?
- G. Rubin It is less than 1000°C.
- E. Hemmelman I do not recall that test method ever being published.
- D. Beckley We are up in the 1500. There is a vacuum pyrolysis technique that has a factor that is used in this program for laminates. You are basically looking at another technique that produces not only a resin content number but also turns around and separates the fiber from the filler and gives you an opportunity to get three numbers out of it.
- E. Stokes The last thing that we did was to look at the 95 percent 13-hour digestion of the specimen. The filler recovery is much higher than expected. Of course, the fiber recovery is down. This is due to the breakup of the fibers and the breakup of filler to the filter. The interesting thing is that of all the solids recovered, more than 51 percent of the expected recovery which indicates that the fiber and filler were, for certain fibers, dissolving or trying non-solid material during the process.
- E. Hemmelman What is that percent based on?
- E. Stokes This is based on all that previous data where we said that there was 51 percent fiber content in that material and 15 percent filler content.
- E. Hemmelman But is that on the prepreg?
- D. Beckley He takes a pure panel, puts it in the flask, runs the temperature below 70°C, and gets a theoretical recovery at the rate that agrees with what he thought he put in, namely 51 percent fabric out for 51 percent laminate. If he raises the temperature to 95°C, the recovery for that species goes down.

- E. Hemmelman How do you know that you have 51 percent fabric in your cure test panel?
- E. Stokes Going back to the graph in Figure 4, anyone can see that the amount of the digestion remains constant over all this time here. Therefore, we are assuming that this is strictly fiber.
- D. Beckley His weight loss slope for number of hours was resin loss and it was pretty constant. Then suddenly it flattened out and stayed at 51 percent, which was recovered amount of fabric. But if he goes too high in temperature or too long a time, the fabric yield goes down. He is dissolving fabric because nitric acid apparently can dissolve this kind of fiber above a temperature threshold.
- E. Hemmelman I still have difficulty with that. The amount of fabric does not have a particular test specimen if he how the test specimen was cured.
- E. Stokes These were all taken from the same panel and the same block, which we assume has the same fabric content.
- E. Hemmelman But do you not know what it is?
- D. Beckley He made a panel that was 16 mill ply thick, so he had basically a fairly coarse panel (probably no flow, not well consolidated), but he weighed the panel, and essentially he knows that he had a ply of fabric in each one. He should have had and I think that that is my inference in that. It would be nice if you and I were sitting with the area weight of the panel and the number of plies and say that that does indicate that amount was there. But we would assume that there is a weight loss and then a crack, and that is the number that he recovered as fabric. He physically got that back in his hands and said that 51 percent of what he started with is a piece of fabric; that agrees pretty well with what he expected the resin content to be. The complement of that is resin plus filler, which agrees pretty well.
- E. Stokes We looked at many of these fabric recovery under SEN2 and all we could see were the fibers.
- T. Bhe Eric, under what conditions are these duplicate or triplicate samples? If you run 2 or 3 samples at 20 hours and 700°C, what would you expect?
- E. Stokes We have done some of that.
- D. Beckley At 20 hours and 67°C, you would get 54 percent. At a higher temperature, you would get to where you wanted to be. That is not a long enough temperature time extraction; that is

too much extraction temperature time. There is one band that gives you the answer that you should get.

T. Bhe If you stay with 20 hours at 65°C, your first value would be 54.73. If you run the second test at the same conditions, what variations would you get?

E. Stokes We looked at the feasibility within this zone (Fig. 4). Outside this zone, if missed by one half hour, the variability would be greater because resin is moving. Here is a fairly constant condition; the resin is gone and the fibers are just wet; nothing has changed. We ran 3 specimens in this zone and got 51 1/2 percent \pm 2 percent. From this we concluded that the nitric acid digestion could be used to quantify the absolute amount of fiber fillers. The digestion at temperatures at or below 70°C are required to qualitatively recover carbon fiber. Digestion at temperatures above 80°C results in visible fiber pitting; digestion at temperatures above 80°C resulted in some chemical dissolution of the carbon carbon fibers. Digestion of carbon phenolic by nitric acid is sensitive to the moisture content composite. To eliminate this sensitivity, I recommend a digestive time of approximately 48 hours and 70°C. Some of the advantages of the procedure are that the procedure requires a small amount[225a procedure r labor intensive, can be done with a little amount of training, and the procedure is nearly insensitive to modern fluctuation of temperatures.

Some of the future work that we are going to do is to look at different filter sizes to see if we can recover a little more filler and then look at the pure resin to make sure that we are not somehow trapping some of the resin residual in the carbon fiber and filler. Then we are going to use the SP28.

T. Bhe How do you define a pure resin?

E. Stokes We have some pure resin blocks made up. (group discussion by Hemmalman and Turbak about pure resin).

A. Turbak Has anyone looked at trying to sulfanate out this phenolic and convert it to a water soluble ?

D. Beckley Are you saying sulfuric acid or....?

A. Turbak With SO₃.

D. Beckley I have never heard of it being attempted.

A. Turbak You may not be able to do it. I know that you can sulfanate the black carbon in tar because I have done that.

P. Pinoli Eric, you have recovery of filler from cured carbon and phenolic composite; the "as received" filler concentration levels and fiber lengths--where do these numbers come from?

E. Stokes That is percentage of the initial weight.

B. Hall Those are preweighed?

E. Stokes These are preweighed specimens that went into the digestion.

B. Hall How do you take care of the moisture content? You mentioned that it was around 5 percent. How do you ...

E. Stokes Regularly, we monitor the specimens. The moisture content cannot be taken out and the filler digestion be done, so we do sister specimens to determine what the moisture content was in our dried and "as received" materials.

P. Pinoli To reiterate my question Eric, what you did is weighed the fabric before you started?

E. Stokes Those were done dry. We dried the filler and the fabric and made up our own samples. We had some pure TCA3 fabric and had the fabric that had not been put in the composite.

D. Beckley There is no resin in that....?

E. Stokes Correct.

C. Heinze I want to mention the information on page which discusses the recovery of the filler 34-B, 35-3, 31-3, 25-2,...

E. Stokes Those are composite specimens.

C. Heinze So you started from scratch and made these. Do you see the "as received" fiber content at the end of the column?

P. Pinoli That was a preweighed out amount of fabric.

E. Stokes No, this is fully cured material.

C. Heinze That is my next question. With these numbers then, did you draw this curve?

E. Stokes Essentially, yes. The same numbers there are 50.5.

C. Heinze The curve and these numbers, which was first?

E. Stokes The both occurred at the same time. Those numbers are these numbers (referring to Figs. 4 - 8).

C. Heinze How do you know that it is 51 percent fiber?

- D. Beckley The starting laminate weight is 100 grams; he recovered 51 grams of fabric, 13 grams of filler, and the percentages....
- P. Pinoli ...and selected those digest times in temperatures.
- D. Beckley Right. The yield was 13 grams of filler and 51 grams of fabric, and he had a 100 gram laminate (he is giving you these round numbers) that became those percentages.
- B. Hall I see that on the agenda that we should have an open meeting, discussion, and recommendations. The only one that I can think of is the recommendation that we support Fiberite and U. S. Polymeric in their investigation of that resin ultrasonic test equipment. Does everyone agree that our official recommendation is to support those two in their continued evaluation of that particular piece of equipment for resin content.
- D. Beckley We need to tackle the carbon assay, though. Did we come up with something on that?
- P. Pinoli Yes. We are going to institute some round robin testing, and I will work with the 3 carbonizers involved, who usually work great together. I will also work with Lou Ann.
- B. Hall These recommendations go out as a committee recommendation, so everyone should indicate either yea or nay. We attach a list of attenders to the recommendations and indicate that these are the recommendations of the committee. Is there anything else that was brought up today that needs action on?
- T. Bhe I would like to hear from Lou Ann about the GPC work at NASA. Are you continuing it now?
- L. Fikes Well, I am working on a different program from Tom with our GPC. The degree of advancement is not what we are looking for. We are just doing characterization studies on prepreg materials. There is no standard acceptance test on GPC for carbon cloth phenolic prepreg.
- B. Hall Is there anyone else?
- M. Towne You know that as I mentioned, Bill, I would like to bring up the subject of density measurement, something that this committee should be considering.
- B. Hall Sure.
- M. Towne I think that with the current system, you may be able to get by, but as you move into higher carbon materials, then it becomes a real problem in how you measure density. These are 3 density techniques that are used for fibers in the industry. This is the test method used for all high modulus

fibers somehow or another (Fig. 12). We use chlorobenzene as we measure it. It is not a really nice thing to work with in the high modulus fibers. When you get into the lower modulus materials, then water presents a problem. This was the study that we did some years ago and it compares those 3 methods and what happens when the results are obtained. These results tell different things about the fiber. This is in shuttle type material, this is the higher modulus material, and this is WCA. When you use helium, you look at porosity in very fine carbon and get very high numbers. These are also. You can get about any number you want here, depending on how long you subject the material.

- P. Pinoli How long do you wait for pore intrusion or how many runs that you make can develop different numbers?
- M. Towne As you move to the higher modulus materials, you start getting quite a drop off here. When you look at the lar, you are measuring another sized porosity, and this is the porosity that is in pretty good measure of how active your fiber is. You can still get your high number with the standard material and with the higher fired; now it takes a significant drop. Then when you go to the orthodichloro benzene, however, these numbers all come in to being pretty close to one another. They do, indeed, represent what you get in composite. Now, depending on what you are using this number for, is density trying to tell you something about the material? (tape ended)
- P. Pinoli I see a dichotomy. If we continue using helium and water as a test methodology for measuring the density of fibers, and we put that criteria on the manufacturer, we are limiting the firing temperature that these people can use. We are forcing them to keep their temperatures down. I personally do not think that that is the direction we want to go. I would rather encourage people to do a higher carbon assay product. I think that what Miles is pointing to is the problem. I would like to hear some comments from Don as far as what Hitco's position is on this.
- D. Beckley I have always said that the density of the fiber depends on the medium that you measure it in, and for years I have resorted to using phenolic resin to get the density of the fiber so that I could, essentially, start to calculate what is true laminate density, my void content, and so on. If you use the helium pycnometer on the surface active rayon carbons, you get an inane number. In fact, ours does not even hold still long enough to make the measurement. It literally runs up and down. I think that the VCK class of materials is probably right on the border of being good, and it is great in WCA. You can get a very rapid measurement and the same answer in helium as you get in composite.

- P. Pinoli I do not care what medium you use with WCA because you can get a pretty good number.
- D. Beckley Yes. I guess that I am not certain what your orthodichlorobenzene does on the low modulus materials.
- M. Towne It is too big to fit in.
- D. Beckley It gives a too low number.
- M. Towne The molecule is too big to fit into the , so it comes out very similar to the composite. I think that is the kind of number that Pat gets with benzene.
- P. Pinoli The molecule is big enough that it acts like a composite resin.
- D. Beckley That is coming close to the best choice that we can make. If you really get down to it, the water number is not much good for spec purposes. There is really no use in building a spec range wide enough to say that the fibers are 195 or 175, and as far as I am concerned, it really does not tell you much about the reality of the material in its performance. It was just convenient to use.
- P. Pinoli Would you be amenable to a specification change that would measure the density with dichlorobenzene? I have seen pretty good correlation between those numbers and what I obtain from the gradient column. The gradient column does have one adverse aspect: the column must be used consistently, and it is a little more time consuming. The manufacturers may prefer to merely change the fluid. I think that there may be a time dependency, Miles, i.e., how long you let it soak. I see it in my tests and I am sure that if you let yours set for 24 hours, then your density results will change.
- D. Beckley We really do not want to have to....
- P. Pinoli The only reason that I like to use a gradient column is because I can get a feel for micro pore structure. From a scientific standpoint, it is good, but I do not know if you want to incorporate it into the NASA program, at this time. Gene, what are your feelings?
- G. Rubin Well, you taught me how to use the gradient column and I am accustomed to it by now.
- P. Pinoli You have not had any problems with monitoring fabric manufacturing product.
- G. Rubin None.

- D. Beckley Pat, would you grade the time that you spent with the gradient column equivalent to or less than ???????????? by the standard technique?
- P. Pinoli Less, because you do not stand there and watch it. You stick it in and come back later. I also do not think that you have to use the column continuously. It still works well at time after being idle for 6 months.
- R. Rubin We have excellent aging, years.
- B. Hall We will take that under advisement and check on it before the next meeting. Is there anyone else?
- E. Mills This is somewhat off the subject, but has anyone noticed any fall off in WCA properties over the last 2 years in terms of densities?
- D. Beckley I have done a summary on it. We approached that looking at serf values from 1983 through 1987 and saw the decrease in values in 1987 and 1988, which is the acknowledged time that they changed method measurements. They changed the equipment which changed the method and showed a drop from numbers of 142 to 147 in the time period before 1987 down to 138 in 1987. Then in 1988, the numbers went back up to 141. We took our prepreg composite serf values for the same years and did not get them down to a one-on-one comparison, but 50 numbers in one year, 80 in another, and 100 in another year. We do not see the 1987 drop happening in those composites.
- M. Towne We went back and measured some of those by the old techniques and also by the dichlorobenzene, and we found that the values were consistent throughout that time.
- E. Mills What, then, is your conclusion?
- M. Towne We were embarrassed because it was not caught by the people looking at the serfs because they definitely....
- E. Mills Did it still meet specs?
- M. Towne It met specs, but unfortunately they were not using their statistical process control charts at the time, which now they would catch that and say that something is going wrong. The difference in the equipment was that one required a larger sample, but they did not change the sample size. So in the helium pycnometer, the size of the sample has a large factor on the end results. Once you get down below a certain....
- D. Beckley Miles, are you saying that the erroneous data came from using the helium pycnometer?

M. Towne Yes. In the new equipment, the cavity is a different size for the size of the sample and it just made a difference. When it went to a larger sample size, the values came rose, even though we knew....

D. Beckley So, the percentage of sample in the cavity apparently made a difference in the percent of error that could be created.

(Group discussion about pinkonometer)

M. Towne As Don said, it is a nice, inexpensive method, and you can keep using it as long as you do not change anything. Then we changed the equipment, thinking that it would be able to do more samples. That is what happened.

P. Pinoli This brings up a point for the committee--those of you who write specifications have to be careful about what you tell these people to do as far as testing their materials. If you tell them to use water pinchnomotry, then you have to accept the data generated by that test procedure. These people are guided by those specifications. The aerospace industry is the one who writes the specs that these people have to live by and they may not be happy with them, but you have to perform the tests by the procedure.

M. Towne For your information, we are almost finished with a sample specification of WCA that was partially written by Morton-Thiokol, and ourselves, which we have recently submitted to NASA. In that specification we have dramatically reduced the range on many of the properties of the WCA that have been listed before as mins and maxes. Density is one that has been reduced from 138 to 15 something. Now I think that it is 142 to 147.

D. Beckley That is quite realistic.

E. Mills That is good and I appreciate that, and I appreciate what he is saying about once you establish a test method, you need to stay with that. Unfortunately, where I am coming from is the program that has had standard specifications WCA through 10 years now, and I think that you are going to give me some heartburn in terms of selling it to my customer and to the Air Force in terms of the changes.

M. Towne This is a spec that is really for NASA, how they want it.

E. Mills Yes, and I can also appreciate that from your standpoint as a vendor, you would like to do the same test whether you sell it to CST, ICS, ??????.

M. Towne It is the same test; it is just whatever limits.??????

E. Mills I think that you will find that there will be a problem if you change methods because there is a paragraph in our specs

that says "no changes to the test methods without consulting us."

- M. Towne It was not a change in the test method; instead, it was a change in the piece of equipment. It is supposed to be the same answer.
- E. Mills Is that different?
- P. Pinoli Miles, what is your preferred method for measuring density of WCA? Do you prefer using orthodichlorobenzene?
- M. Towne Frankly, I think that it is more reliable. But if I really want to find out what is the density for a material that I have that will fit into this composite, I would benzene.
- P. Pinoli In the specification that Ed is talking about, how much latitude does he provide you; can you use water in that method, or do you use helium?
- M. Towne I think that one is probably based on helium.
- D. Beckley It is basically spelled out as a "no change clause" so what you are doing is what you are authorized to continue to do. It sounds like you have created a NASA material test series.
- M. Towne NASA wanted to see things tightened up.
- D. Beckley He can let you tighten the numbers.
- E. Mills You can certainly supply tighter numbers if you want to supply 142 to 147 in our spec. I do not know off the top of my head that that says that it is 138 to 135. What concerns me is if the test method has been changed and if our data base is, 146 over 10 years with some deviation, and now you give me a different method that will give me 136 mean for the same data status,, then it would totally wipe me out.
- M. Towne Understand that it was not realized that there was any difference in the test equipment; it was merely the size of the cavity, and the data that is erroneous is that data given to you which we are getting from those low values. That was the earliest data. Unfortunately when that equipment looked like it was the same sort of thing, this is what you buy to do helium pycnometry.
- E. Mills To a large degree we have controls in specifying equipment, and I think that for some of the parameters we have as many as 2 alternates which are considered to be equivalent; I am not sure that Fiberite and U. S. Polymeric would agree that there are alternates.
- P. Pinoli I have never seen specs that really address that. For example, they may list a piece of equipment and say that it

is equivalent, but I have never seen a test method tied up to a piece of equipment.

E. Mills There are a couple that are more specific than that that Boeing helped us with.

M. Towne A good example that we talked about today is the spec that calls on the Dupont 99.

(group discussion about this spec)

D. Beckley Apparently it should not be continued and supported either in that instance. Do you specify a density range and then does your fabric spec allow water displacement?

E. Mills I think that you will find that a tightened spec is a little bit broader than the IUS spec, but I would have to go back and revisit them and obviously we will do that. The bottom line is having an established test procedure. You and I went through this with some degree of cure with Kaiser involved. After having established a procedure, we would be concerned about any changes that would be made without someone blessing them or doing a round robin.

M. Towne Curing comes into the category with one little piece of equipment; what do you do when you replace that?

E. Mills I know. There is a certain amount of reasonableness in it and unfortunately this industry is maybe driving it a little bit beyond the extreme in the other direction in taking the flexibility out of your test method. But you can understand why when you get this sort of thing happening as you have an example up here, I am now going to have to go back and explain to my customer why I do not have density data that is consistent with what he thought he had a data base for. You can make an argument that those things do not have an effect on density or that your new test method is more representative. There are new test methods that do, in fact, give you a better value of a given parameter than the old methods and a more real number.

M. Towne I think....

E. Mills All I am saying is that if we start changing things, we need to talk to each other and understand what we are doing so that there will be no surprises.

M. Towne I think this is inherent in the industry before SPC. These are the things that we hope now to catch when something like that creeps in. I think the change from the old equipment to the new equipment on about any material that you would measure would have proven that this is the same equipment, the same technique. There is nothing different; it merely happened that on WCA the size sample that they

were using is going to make a difference. Unfortunately, it was tested out and compared on a pitch material and it did not make a difference.

- E. Mills I seem to keep coming up against a degree of cure problem at one of my other vendors. We have data for FM5064 that shows degrees of cures in the 98 to 99 percent range, and Don tells me that that is not credible, but I have 30 or 40 data points, circa 1983 to 1985 or 1986, none of which violate that. Then I get very critical and start looking at it. I think that I probably have a more realistic test now, but I am coming in the 95 ± 2 percent range, which is where Don tells me I should be.
- D. Beckley Talking about FTM..(Mills and Beckley both talk at the same time--conversation is inaudible).
- E. Mills It is something that has been locked in the standard for, in this case, 10 years. In the case of Titan plane, 25 years has been an industry standard.
- D. Beckley Is it as good as the ASTM would lead us to believe?
- E. Mills I am looking at a data base that has a fairly low standard deviation and it has those numbers.
- E. Hemmelman How do I know that that is a bad test?
- E. Mills It is the same thing. You check out your test with pitch and it is okay and maybe it is not okay. Now we have a round robin going to run approximately 6 (it may have expanded to 10 or 12 specimens) in 10 or 12 labs, and we are going to try to all that. If it is a bad test, then we can have the data that will say exactly what it is in that test.
- D. Beckley We have encountered a problem for the group to think about. If there is a cured laminate (this piece of material), and for the test to be run, it must be comminuted. It has to be broken up and ground down into something that is more extractable so that a fluid can get in and attack it. If the composite is merely ????? then a limited amount of surface occurs and no answer is found. The particle size must be obtained, and the way that this is done is to use a machine tool and get some shavings in the process from the very point contact on the machine tool. Then some additional material is cured and the end result is that the 98 number reproduced time after time. From our experience we can take the heat resin in the laboratory, not mess it up with fiber and filler, and find out that it only produces a 95 percent number; therefore, we know that 95 percent is the right number. When we see people reproducing the process and getting a 98, we have to assume that there is a reason for it; it sounds like this machining issue is what is producing

the number that is repeatable , but it is not the correct number.

E. Hemmelman Would the 95 percent on heat resin be about the same as 98 on

D. Beckley No, I am making the correction. I am saying that the equivalent of a 95 number and the system is designed not to have a complete cure. It is a carbon carbon resin, and we like some degree of freedom up to 700⁰ for the atoms to re-orient themselves, so it is supposed to have a high extractable number after a 325 cure.

E. Mills I was merely pointing out that a test has been conducted over a period of years in an established data base and then suddenly the test is improved. Now I, as an intermediate vendor, will have to sell my customer--the Air Force or NASA or Boeing or whoever that happens to be--on the process. Justifiably, they are concerned.

P. Pinoli Morton Thiokol Elkton reported WCA at 1.38 specific gravity. I questioned if that sounds reasonable for WCA and I would be concerned. From all the data that I have ever seen on the WCA, I would be concerned. I have never seen anything that low. Something has happened to that fiber, something that is making it uniquely different. Now, it turns out that it was test error that was introducing those numbers. Elkton made the comment that "we do not like surprises." What you are saying, Miles, is that we made a mistake in our laboratories and someone should have picked that up.

E. Mills We are just as guilty in that we look at the serfs and Kaiser looks at the serfs in between and then we do not pick it up until all of a sudden we see a low density problem on the end. Then we start retracing our steps and we should have been doing our homework as we went, as opposed to waiting to the end.

M. Towne Don caught it and confronted us with it, but he had not seen it in what he was putting out, so we did not get excited about it.

D. Beckley It met his specs.

E. Mills You are telling me then that I thought I might have had a correlation and you have just eliminated it. I am really upset with Miles now. Actually I would rather hear him say that the product has not changed. There was some concern that there may have been a change in fiber source. Granted that is a pre-Avtex problem but that cropped up as being a potential, which we were very concerned about. So, I am glad to hear that it was the test method. It is much easier to live with when I have exit cones to produce.

- P. Pinoli I have learned that manufacturers seldom have a separate set of standard procedures to test their materials to. I had hoped at one time that they did. In other words, I hoped the carbonizers tested to a higher standard than what they tell you. Miles told me, when I asked him what was a VCK, that VCK is what your specifications says it will be. They do not have any secret file of specification requirements for VCK, but if you call out a product spec, they will produce that material to meet that specification. The guy down the street has a slightly different specification and they will produce a VCK that will meet it. You must learn the name of the game which is that you have to write a specification to meet your requirements. Whether it is right or wrong, that is the reality of the situation.
- E. Mills We do that and we recognize that they quite frequently know more about their process than we do, a lot of which is proprietary. Obviously and understandably, I do not expect them to tell me all of that and I do not expect them to put it into spec; that is why we put the "no changes" paragraph after its qualified for use. We do not expect to see changes in the materials, and if there are any changes, and then the vendor goes out business, then come tell us. If you want to make a change in something else, we need to discuss it. That is pretty much the way it has to be treated from the standpoint of if I start putting everything in the spec that controls exactly the product, that spec would now be a proprietary document. It would also be something that I could not do what I do now and that is to have both U.S. Polymeric and Fiberite qualified sources for a given material or given end item.
- Incidentally, that brings up one other issue that I just got into with my local Air Force representative. Maybe someone can help me out with my problem. I specified yarn to 300 yarn in a spec and the title of the spec is "polykrillonytrilly yarn." Air Force tells me that I cannot specify only being only Amoco as manufacturer because that violates Federal acquisition regulations. They say that I have to accept any polykrillonytrill yarn, otherwise, I am violating the law.
- F. Turbak Did it meet the specs?
- E. Mills The specs are generic. It meets the tensile strength, the modulus, strength failure, density, etc.
- F. Turbak Can you use bits of higher specs to meet him as the producer?
- E. Mills What I do is qualify the sources.
- D. Beckley You have a qualification paragraph that says the materials must be offered for inspection and meet the criteria and

Justification that no one else offered the material at that time.

- P. Pinoli You are saying then that the Air Force is saying that you cannot specify polyacrylonitrile precursor?
- E. Mills I have one air force, namely Aerospace, and the Air Force is coming in and saying that the general is telling me that they do not want any changes. In fact, they want torry manufactured yarn that is imported. That is what we built in 1981. Then I have the local retired Air Force guy who has come in as a government QC guy and tells me that I am violating acquisition regulations. He is more of a bureaucrat than an engineer and almost more of a bureaucrat than a customer, but I have to deal with him. I referred him to his Aerospace . I told him that they could work it out and tell me what they wanted and I would build it. I think Don may have the answer--if the wording is right on the paragraph, I do not think it was in case, I will have to try that anyway.
- T. Bhe Generally, at the end of the spec you would have your modified project list that identifies?????.
- E. Mills It depends on, for instance, if you have a Navy spec; the GPLs are totally different. The GPL is not controlled by engineering, but it is controlled by quality. It provides for some interesting debates, but unfortunately they do not produce much work. They produce numerous of debates.
- T. Bhe I have one more comment. Let us say that on the fiber density you specify 1.35 to 1.5, and the supplier comes in and tightens the spec from 1.42 to 1.47. Would you have any problems with that?
- E. Mills I would be happy if he tightens it as long as he does not change his test methods and as long as my data base is consistent with what he tightens his to. In fact, we just did that on the 2300; we worked it out on a previous data base which had a previous spec limit of 370 or something like that. Then we raised it to be consistent with the spec, but we never used any material over 100 blocks. We had never seen anything below 430 or something like that until we raised it, figuring that if we now at 370 and the average is 500 and the lowest that we have ever seen is 430, then we are concerned. Yet it is not. It is not as rigorous a statistic process control as what I would like to get into it for it to be more effective. Some of the vendors argue ??????? , and we are very glad to see that. In general, with those caveats, I would like to see a tighter band. Amoco, U. S. Polymeric, and Kaiser, probably all have their internal bands and I think that our product is tighter than what we were requiring in many cases.

- T. Bhe As long as the supplies do not raise the price?
- E. Mill It does allow them the flexibility to evaluate one that comes in below their requirements and we can buy it. Sometimes we do not catch those, but we hope that we catch them all.
- B. Hall Please do not forget to turn in your badges. We appreciate everyone being here, and you will be hearing from us in the very near future.
- ADJOURNED 4:50 P. M.

APPENDIX A

DICK HERMAN'S PRESENTATION

SPIP/NOZZLE TASK 3.2

OVERVIEW

PRESENTED TO THE TASK 3.2.1.1-2

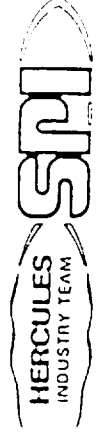
EXECUTIVE COMMITTEE

16 MAY 1989

R. M. HERMAN, PROGRAM MANAGER
HERCULES AEROSPACE CORPORATION

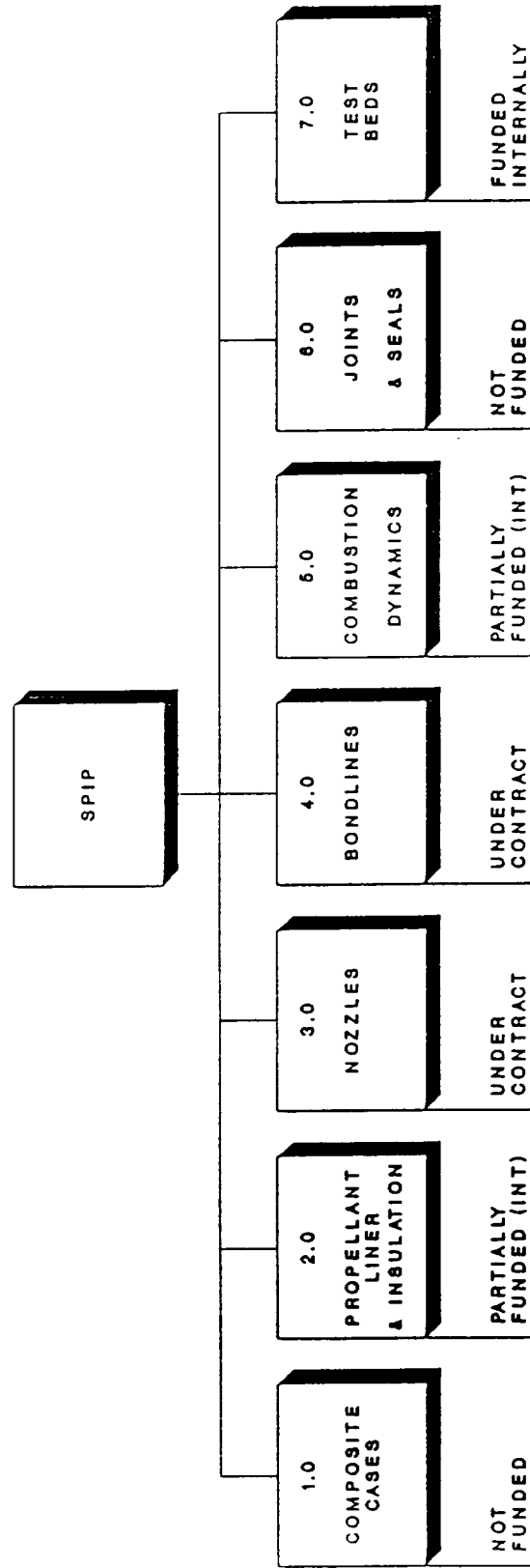
SPIP-7

0902S



SPIP/NOZZLE PROGRAM OBJECTIVE

- THE SOLID PROPULSION INTEGRITY PROGRAM HAS BEEN ESTABLISHED TO IMPROVE THE SUCCESS RATE OF U.S. BUILT SOLID ROCKET MOTORS BY IMPROVING THE BASIC ENGINEERING UNDERSTANDING/CAPABILITIES OF THE SYSTEMS.
- SEVEN INITIATIVES HAVE BEEN IDENTIFIED

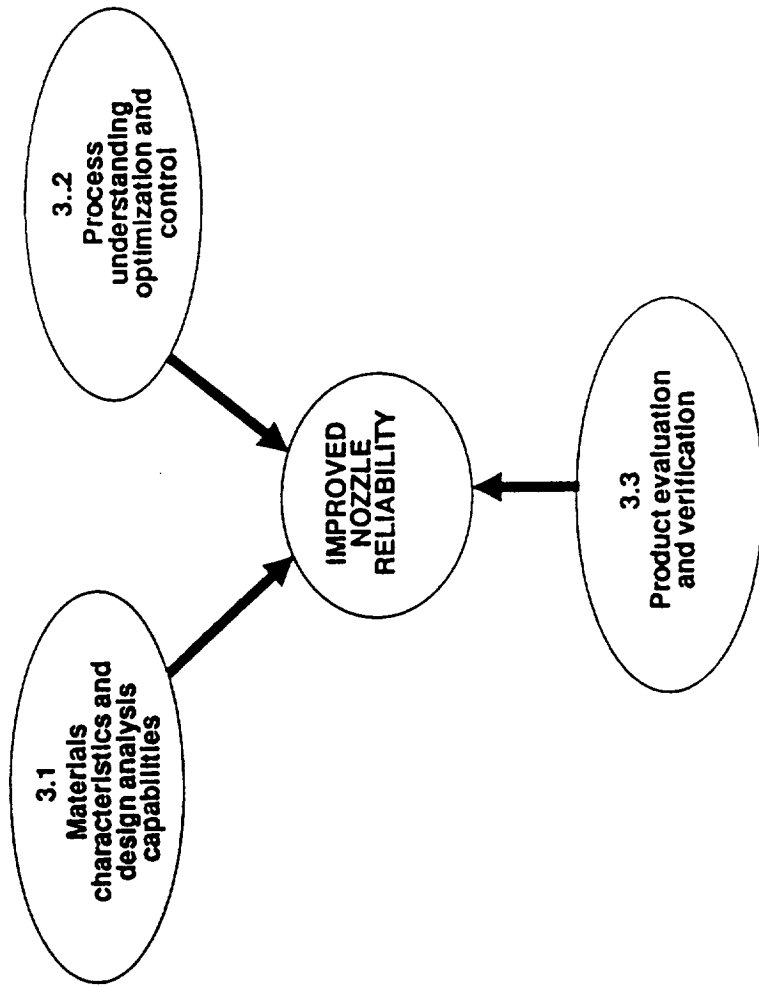


SPIP-5

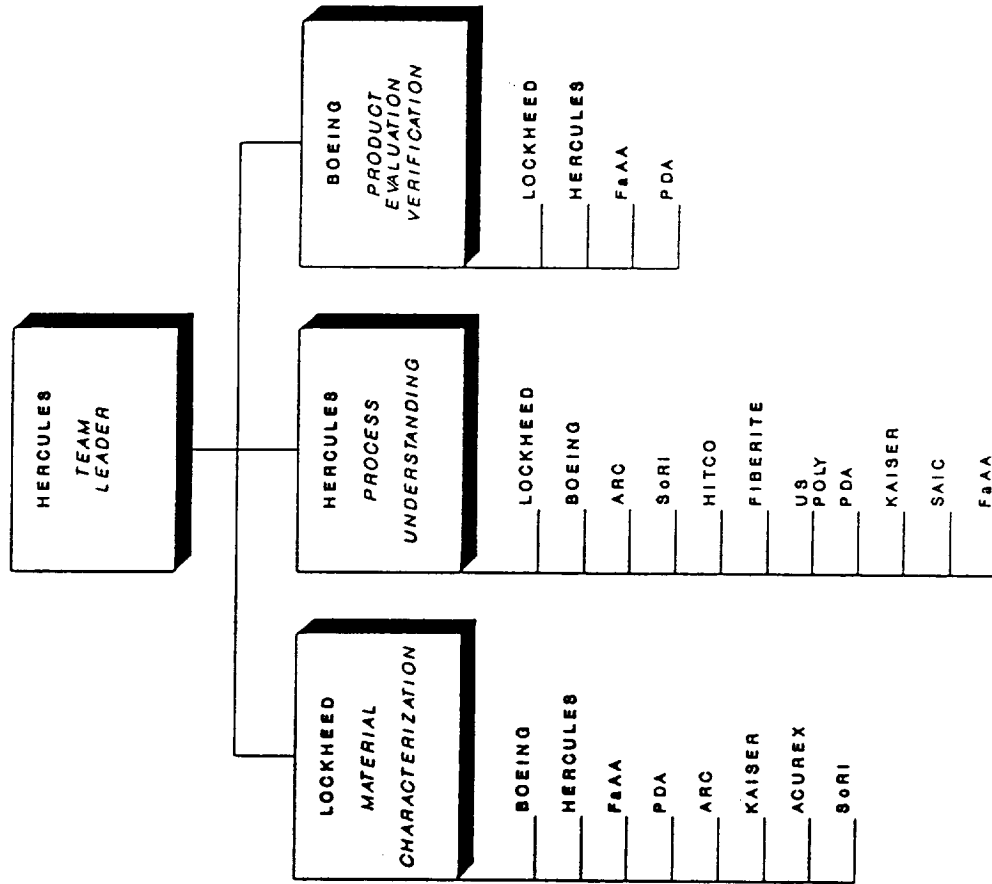


NOZZLE SPIP TECHNICAL OBJECTIVE

TO IMPROVE THE OVERALL SUCCESS RATE OF U.S. BUILT SOLID ROCKET MOTOR NOZZLES BY
IMPROVING THE BASIC ENGINEERING UNDERSTANDING/CAPABILITIES IN THREE MAJOR AREAS



PARTICIPATING COMPANIES (13) GIVE TEAM AN INDUSTRY BASE & DEPTH OF EXPERIENCE



3.2.1.1 CONSTITUENT AND PREPREG TESTS AND TEST METHODS ASSESSMENT - PAT PINOLI, LPARL, PI

OBJECTIVES: ASSESS CURRENT TEST METHODS AND IDENTIFY NEEDED IMPROVEMENTS

EVALUATION METHOD: UTILIZE ROUND ROBIN TESTING

STATUS:

- FIVE (5) TASKS IDENTIFIED INVOLVING 4 CONSTITUENT TESTS
 - TEST METHODS ARE INADEQUATE AND/OR UNSAFE (DMF METHOD CARCINOGENIC)
 - THE FIFTH TASK IS THE MONITORING OF SECOND SOURCE RAYON
 - WORK PLANS TO COVER INVESTIGATIONS, WITH COMPLETION DATES, HAVE BEEN DEVELOPED
 - DETAILED DISCUSSIONS ON THE FIVE TASKS ARE AGENDA FOR THIS MEETING
 - WITH COMPLETION OF THESE TASKS IN 1989, ADDITIONAL TESTS WILL BE INVESTIGATED IN 1990

3.2.1.2 C/C EXIT CONE TECHNOLOGY REVIEW - LIZ EMERY, HAC, PI

OBJECTIVES: IDENTIFY THE THREE C/C EXIT CONE TECHNOLOGIES HAVING THE GREATEST
POTENTIAL FOR CONTINUED DEVELOPMENT

EVALUATION METHOD:

- QUESTIONNAIRES COMPLETED BY ELEVEN FABRICATORS
- ANSWERS SUMMARIZED
- INDUSTRY WIDE SCORING BY NON-FABRICATORS
- RESULTS AND RECOMMENDATIONS DUE TO MSFC JULY 89

STATUS:

- QUESTIONS COMPLETED
- SUMMARIES COMPLETED
- DISTRIBUTION FOR INDUSTRY SCORING THIS WEEK
- FINAL SCORING AT HAC BY END OF MAY

0902S^{SPI}-7



3.2.1.3 PAN BASED ABLATIVE EVALUATION - CHARLIE HEYBORNE, HAC, PI

OBJECTIVES: IDENTIFY BEST PAN BASED MATERIAL SYSTEMS FOR 1) THROAT, AND 2) EXIT CONE

EVALUATION METHOD: UTILIZE LITERATURE, 2 INCH NOZZLE THROAT FIRINGS, MECHANICAL PROPERTIES DATA, THERMAL DATA, AND BRUTUS FIRINGS TO DOWN SELECT. FM-5055 IS THE BASELINE.

STATUS:

- FOUR (4) THROAT CANDIDATES, SIX (6) STANDARD DENSITY EXIT CONE CANDIDATES, AND TWO LOW DENSITY CANDIDATES WERE SELECTED BY INDUSTRY RECOMMENDATION AND AVAILABLE LITERATURE
- PREPREGS OF SIX MATERIALS ARE AT KAISER AND END ITEM SPECIMENS ARE BEGINNING FABRICATION THIS WEEK
- DESIGN OF 2 INCH NOZZLE IS COMPLETED
- AAE IS ON SCHEDULE WITH MANUFACTURE OF REMAINDER OF COMPONENTS FOR FIRST TEST
- NASA IS PREPARING FOR FIRST OF THREE 2 INCH FIRINGS IN JULY, 1989; LAST FIRING OCTOBER 1989

SPIP-7
0902S

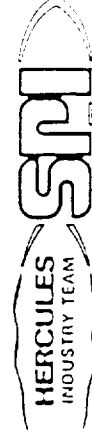


3.2.1.3 CONTINUED

- ASPC IS ON BOARD AND IS PREPARING TO SUPPORT PROCESS OPTIMIZATION BEGINNING AFTER THE FIRST MOTOR FIRING
- BEST THROAT AND EXIT CONE MATERIALS SELECTION AFTER BRUTUS TESTS IN THIRD QUARTER 1990

SPIP-7

0902S



1

APPENDIX B

BILL HALL'S PRESENTATION

Materials Supplier Flow Sheet for Carbon Phenolic Nozzle Components

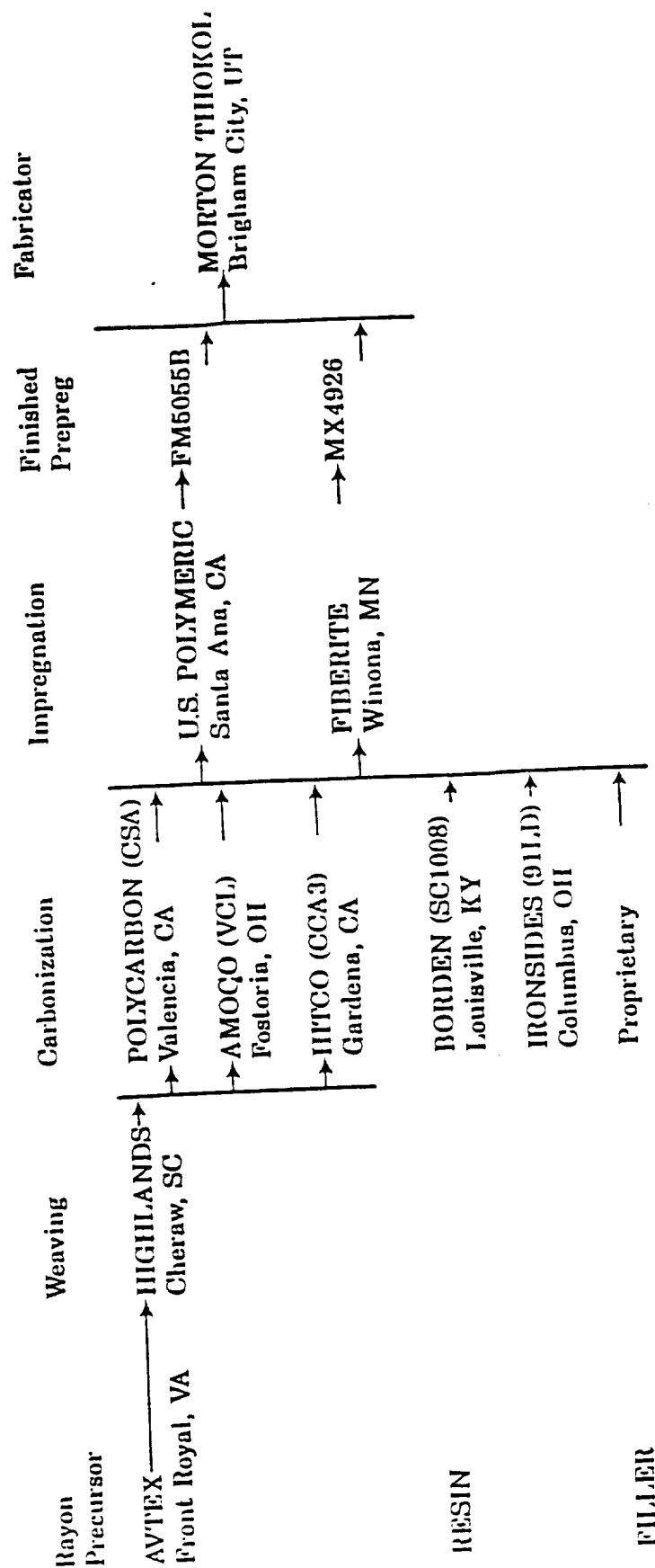


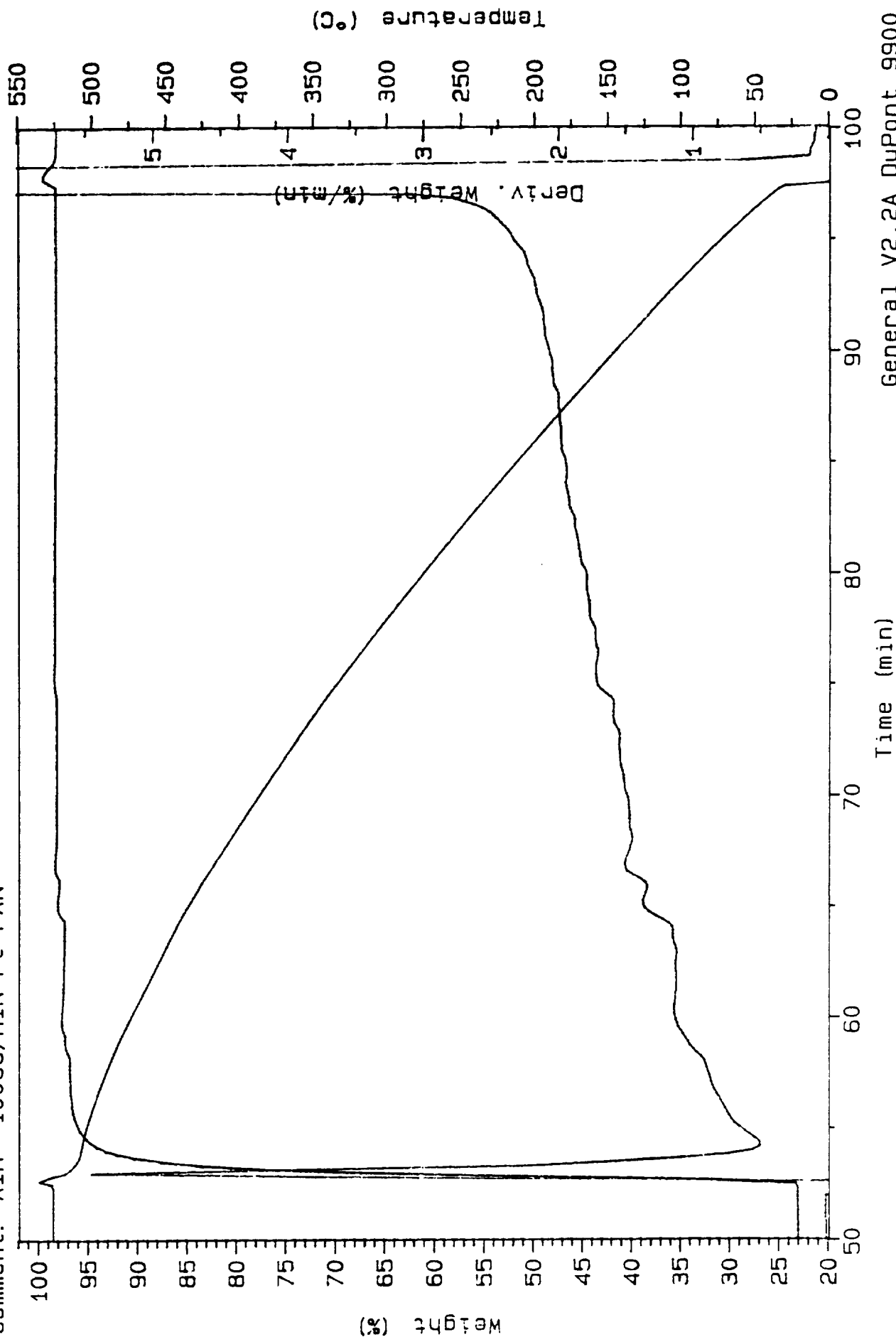
Fig. 7 - 1 - Material Supplier Flow Sheet

APPENDIX C
MILES TOWNE'S PRESENTATION

Sample: VCL 1983 CONTROL 1090 PPM
Size: 16.5520 mg
Method: TGA TEST
Comment: AIR 100CC/MIN Pt PAN

TGA

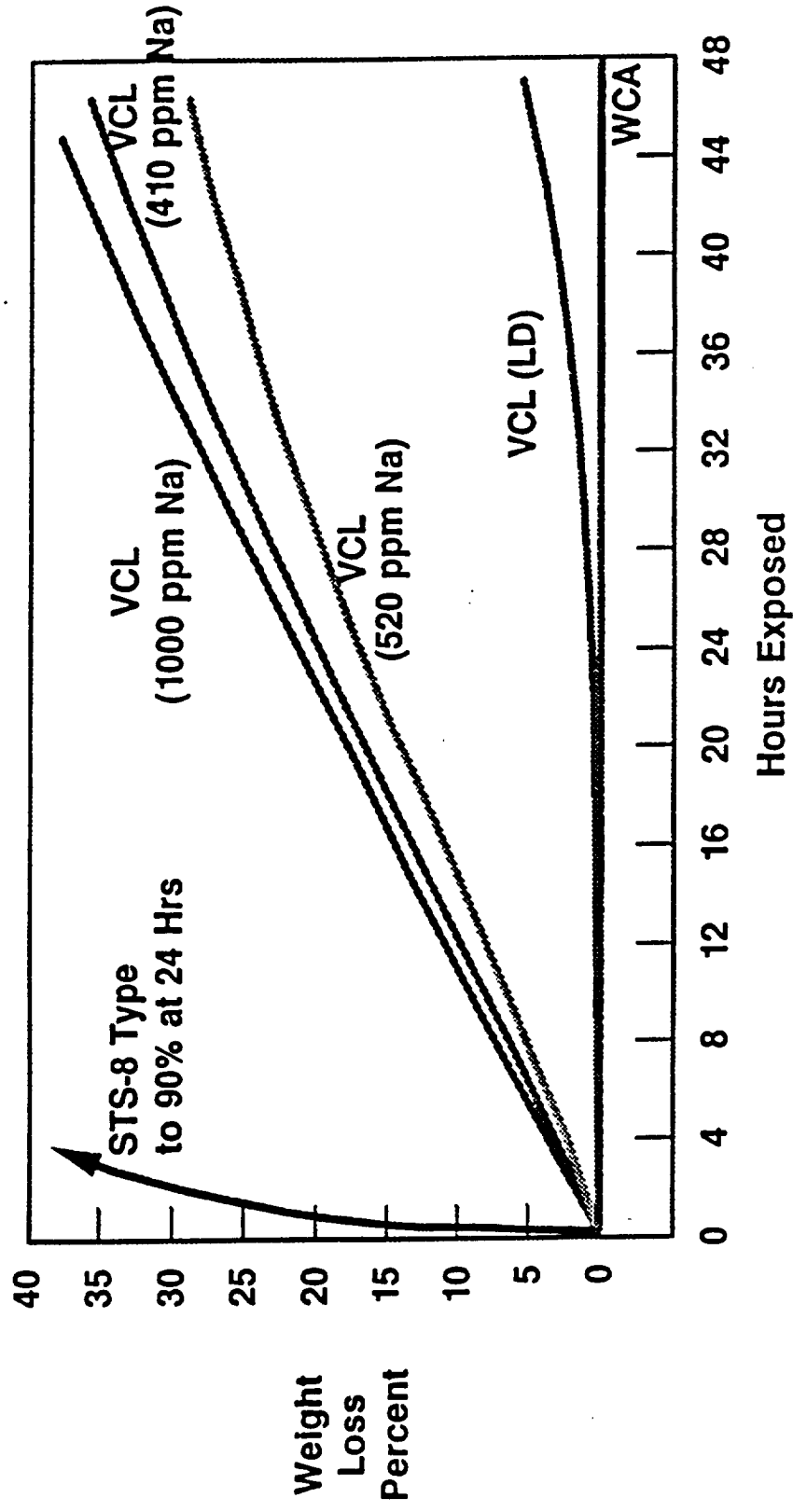
File: VCL1983.99
Operator: MK
Run Date: 05/01/89 11:27



Time (min)

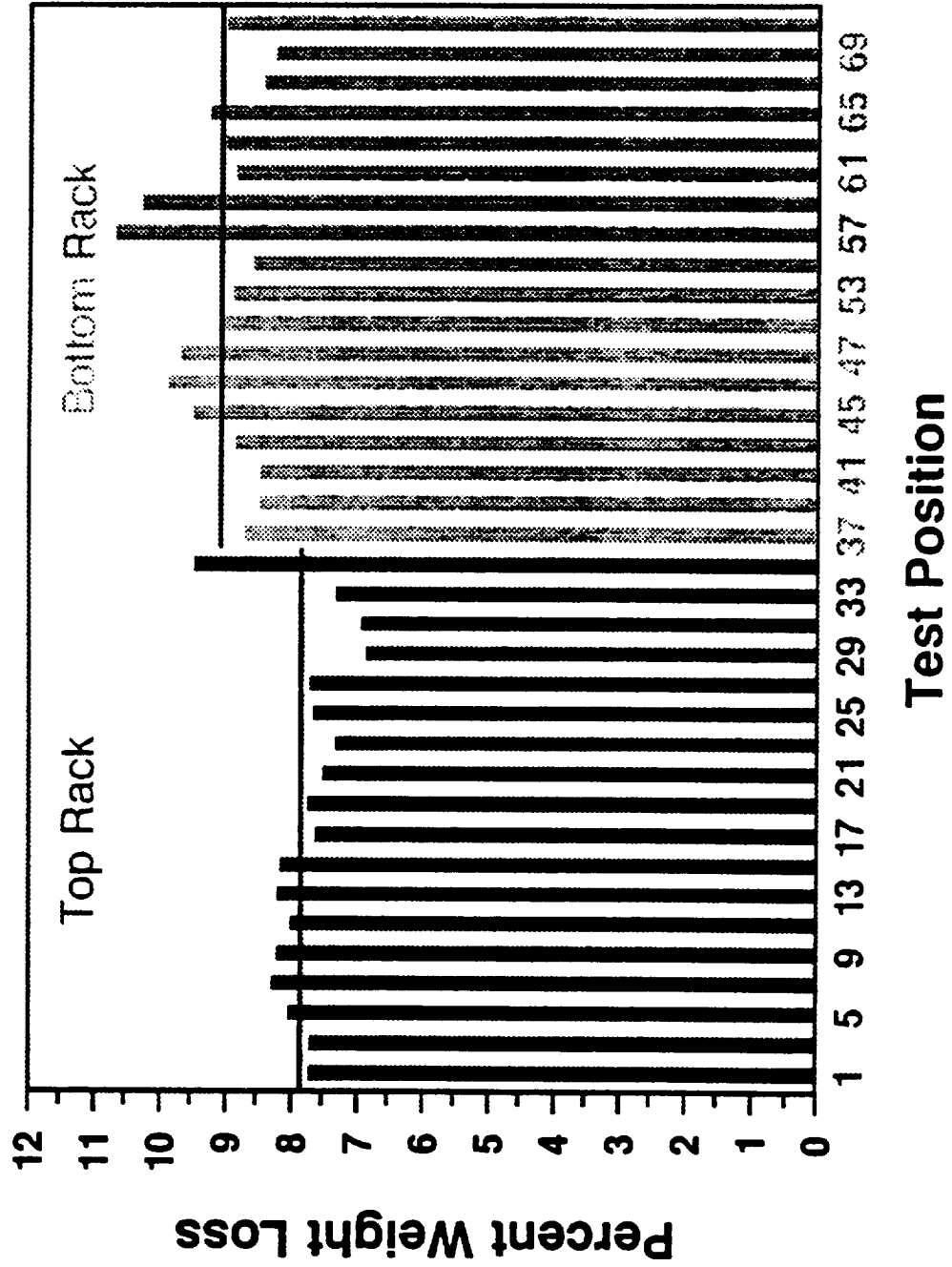
General V2.2A DuPont 9900

OXIDATION WEIGHT LOSS AT 375°C RAYON FABRICS



REPEATABILITY WITHIN TEST OVEN

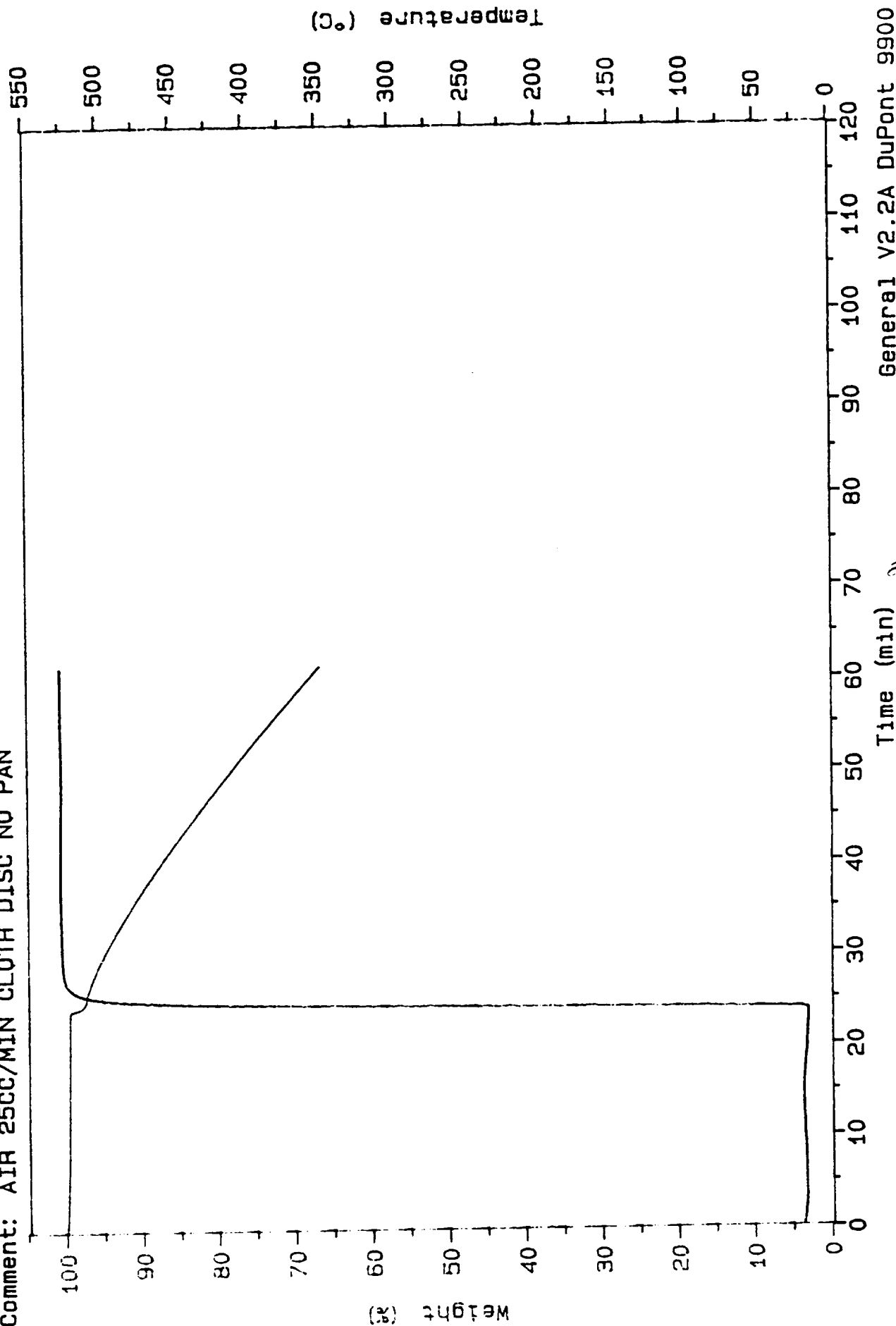
T-650/35 Fiber



Sample: CSA 0539
Size: 14.1020 mg
Method: TGA TEST
Comment: AIR 25CC/MIN CLOTH DISC NO PAN

TGA

File: 89050111B.03
Operator: MK
Run Date: 05/10/89 10:23



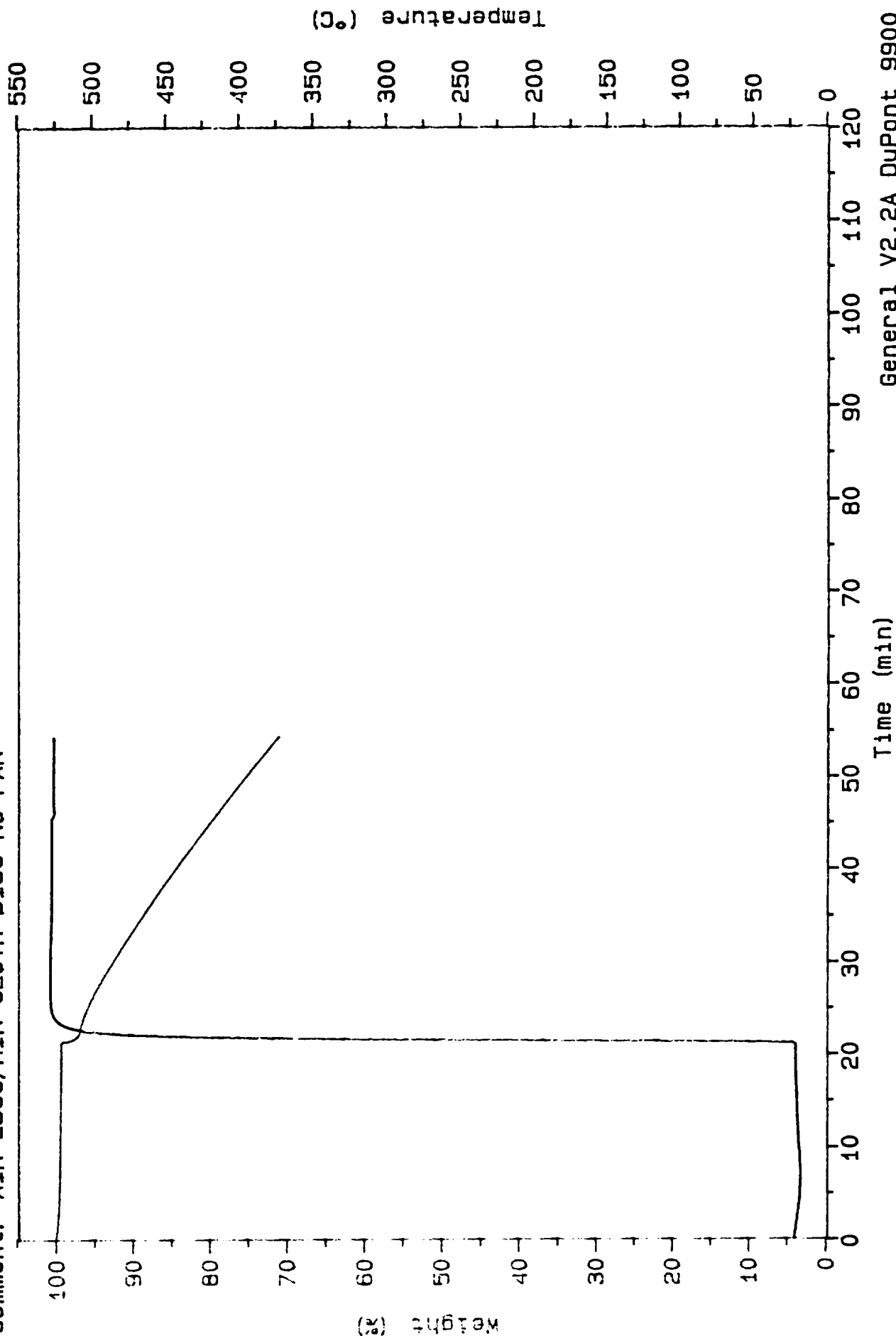
Time (min)

General V2.2A DuPont 9900

Sample: CSA 0567
Size: 15.8270 mg
Method: TGA TEST
Comment: AIR 25CC/MIN CLOTH DISC NO PAN

TGA

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Operator: MK
Run Date: 05/10/89 12:16

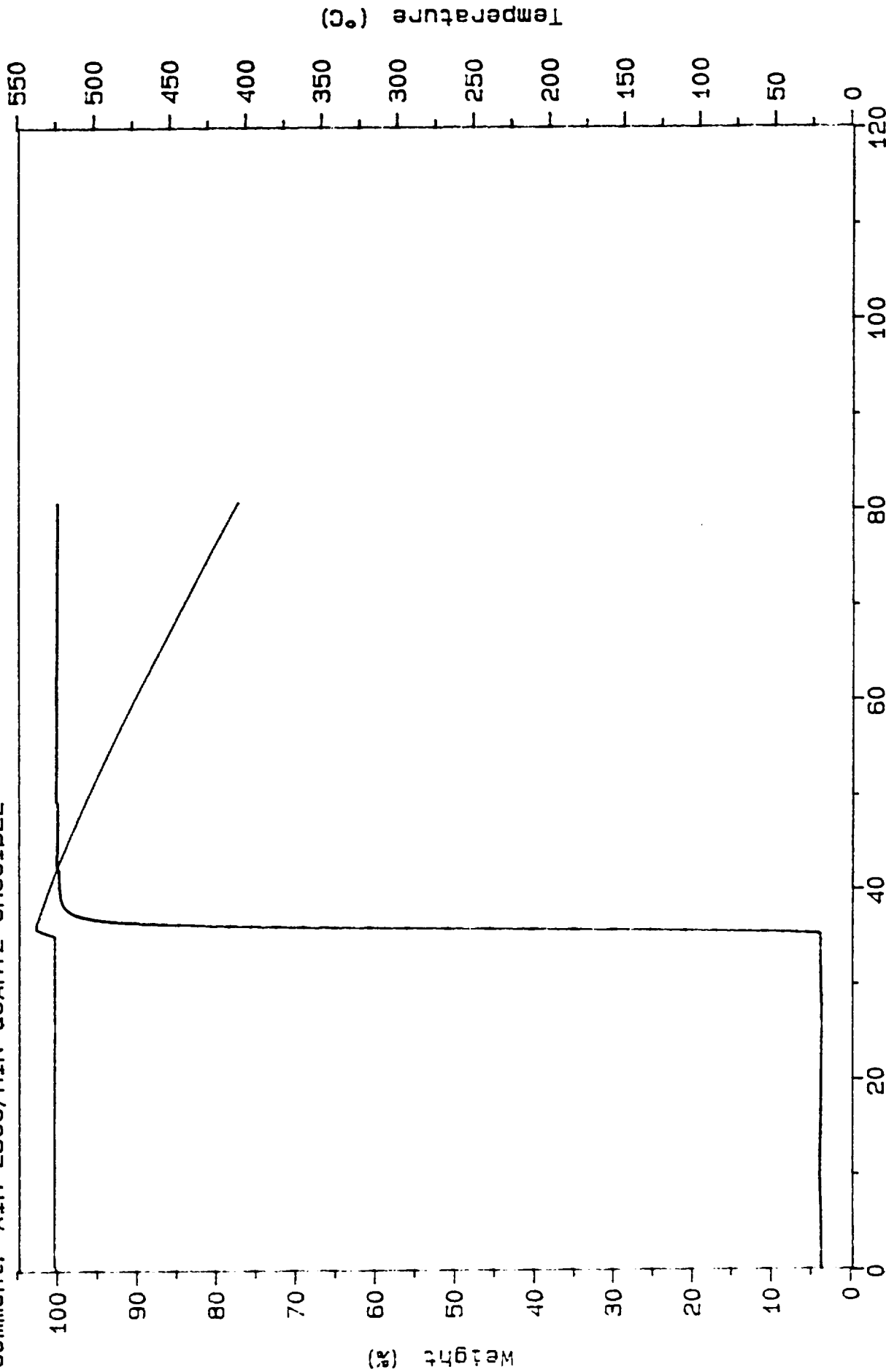


General V2.2A DuPont 9900

Sample: AMOCO UCX-13
Size: 3.8630 mg
Method: TGA TEST
Comment: AIR 25CC/MIN QUARTZ CRUCIBLE

TGA

File: 89050111H.01
Operator: MK
Run Date: 05/09/89 07:10



Time (min)

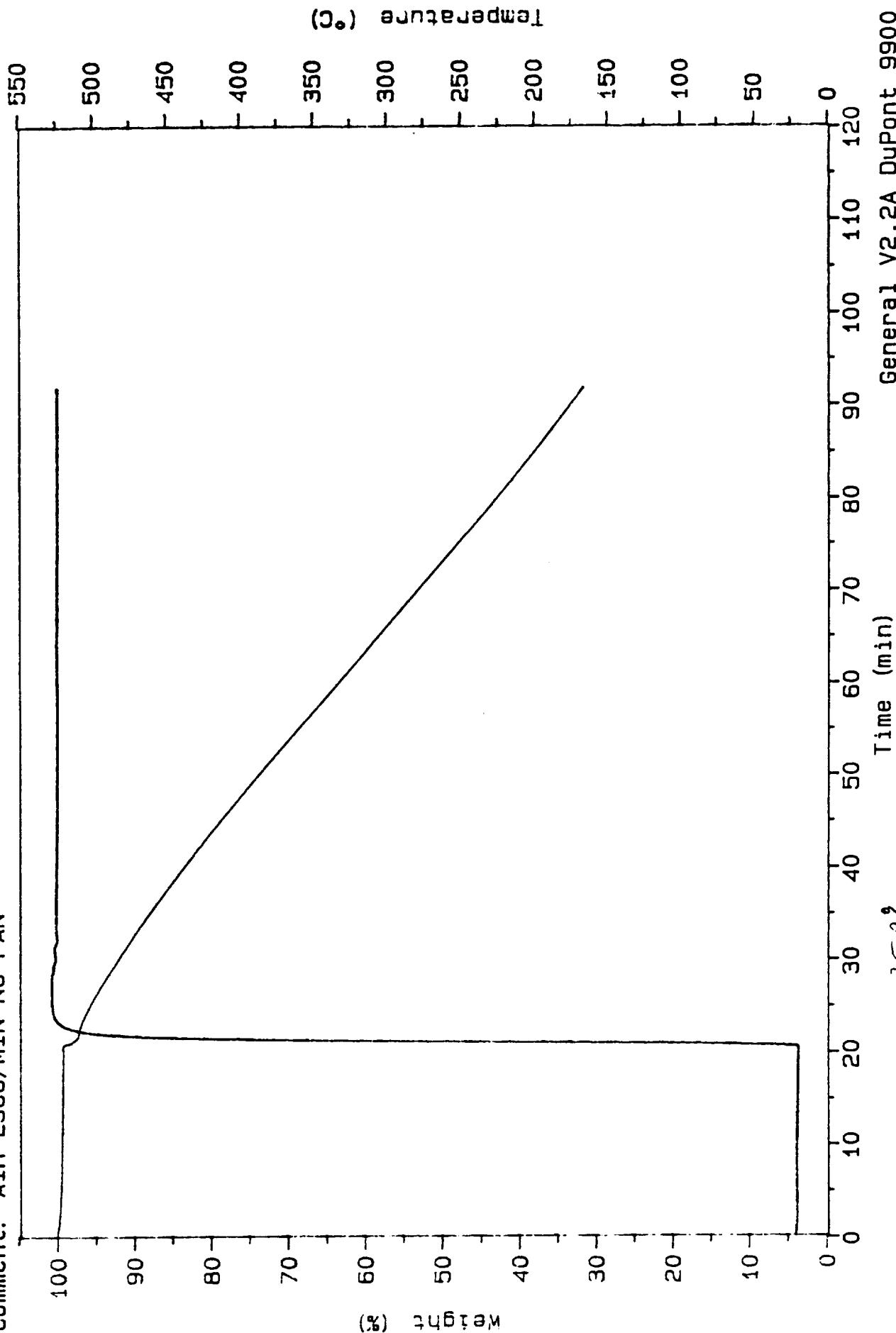
General V2.2A DuPont 9900

16.8%

Sample: CSA 0534 CLOTH DISC
Size: 14.9730 mg
Method: TGA TEST
Comment: AIR 25CC/MIN NO PAN

TGA

File: 89050111A.04
Operator: MK
Run Date: 05/08/89 12:39



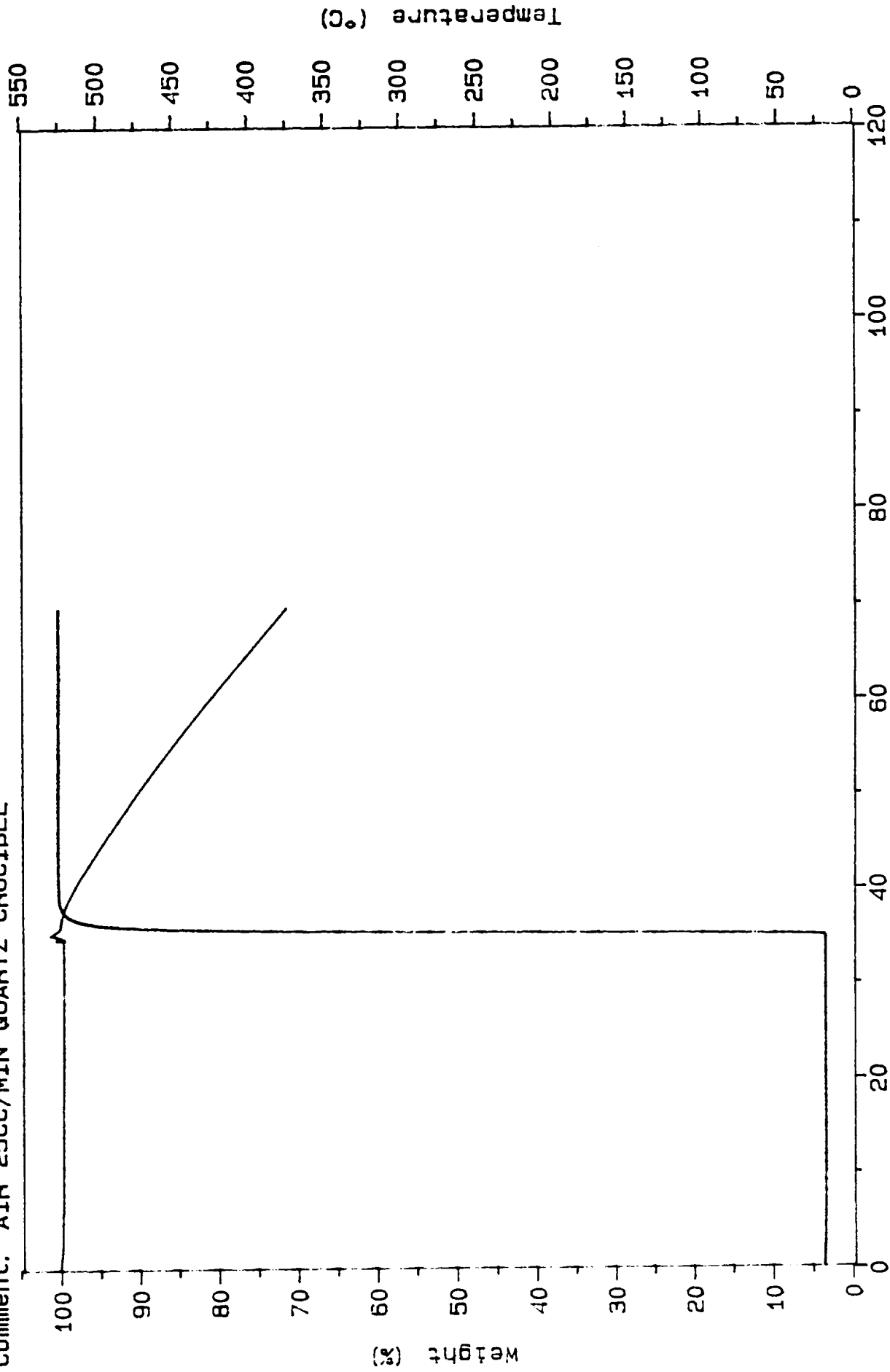
25.8%

General V2.2A DuPont 9900

Sample: CCA-3 42099
Size: 4.4540 mg
Method: TGA TEST
Comment: AIR 25CC/MIN QUARTZ CRUCIBLE

TGA

File: 89050111E.01
Operator: MK
Run Date: 05/09/89 08: 44



Time (min)

General V2,2A DuPont 9900

N E C / A P P I

CARBON ASSAY - FOSTORIA PROCEDURE

ASTM D3178 CARBON AND HYDROGEN IN THE ANALYSIS OF COKE AND COAL

NOTES: CO₂ COLLECTION IN ASCARITE II
FUSED LEAD CHROMATE OMITTED
SAMPLE DRIED 30 MINUTES AT 110°C IN VACUUM
SAMPLE SIZE 0.10 - 0.15 GRAMS - NOT MILLED

TEST RESULTS - REPRODUCIBILITY

VCK	99.76, 99.57, 99.65	AVERAGE = 99.66	S = 0.09
VCL	96.88, 97.04, 96.74	AVERAGE = 96.89	S = 0.15
WCA NO. 1	99.98, 99.95, 99.92	AVERAGE = 99.95	S = 0.03
WCA NO. 2	100.04, 100.07, 100.03	AVERAGE = 100.04	S = 0.02

N E C / A P P I

COMPARISON: ASTM D3178 VERSUS LECO

NOTE: LECO TESTS ALL RUN BY LECO OPERATOR

STANDARDIZATION WITH "LOW CARBON" STANDARD

ACETANILIDE GAVE HIGH RESULTS

SUGAR WAS UNSATISFACTORY

STANDARIZED WITH WCA = 100%

RAN VCL SAMPLE TEN TIMES

AVERAGE = 97.10% S = 0.15

LOW VALUE 96.88% HIGH VALUE 97.32%

RERAN WCA FOUR TIMES

99.97, 100.16, 100.06, 99.95

AVERAGE = 100.03% S = 0.10

RAN VCL TEN ADDITIONAL TIMES

AVERAGE = 96.98% S = 0.14

LOW VALUE 96.69% HIGH VALUE 97.22%

RERAN WCA TWICE MORE

100.14, 99.94

CONCLUSIONS: LECO IS OPERATOR SENSITIVE, FREQUENT STANDARDIZATION
WITH WCA NECESSARY (MORE THAN ONCE PER DAY)

FABRIC DENSITY TEST METHODS

- **ASTM C604** - Test Method for True Specific Gravity of Refractory Materials by Gas-Comparison Pycnometer
- **ASTM C135** - Test Method for True Specific Gravity of Refractory Materials by Water Immersion
- **ASTM D3800** - Test Method for Density of High Modulus Fibers - Procedure A

FABRIC DENSITIES BY TEST METHOD

g/cc

<u>Fabric</u>	<u>C604 He</u>	<u>C135 H₂O</u>	<u>D2800 ODB</u>	<u>Epoxy Composite</u>
VCL (HD)	1.92	1.86	1.52	1.50
VCL (LD)	1.79	1.55	1.49	1.46
WCA	1.45	1.44	1.44	1.44

T G A O X I D A T I O N S T U D I E S

D U P O N T 9 9 0 0 A N A L Y Z E R

FURNACE HEATED TO TEMPERATURE THEN SAMPLE
HOLDER TUBE INSERTED INTO FURNACE

TEMPERATURE RISE IN APPROXIMATELY THREE (3) MINUTES

LOW FIRED SAMPLES LOST MOISTURE DURING HEATUP
AND FIRST TWO TO THREE MINUTES AT TEMPERATURE

T G A O X I D A T I O N S T U D I E S

D U P O N T 9 9 0 0 A N A L Y Z E R

FURNACE HEATED TO TEMPERATURE THEN SAMPLE
HOLDER TUBE INSERTED INTO FURNACE

TEMPERATURE RISE IN APPROXIMATELY THREE (3) MINUTES

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AND FIRST TWO TO THREE MINUTES AT TEMPERATURE

T G A O X I D A T I O N S T U D I E S

D U P O N T 9 9 0 0 A N A L Y Z E R

1983 VINTAGE VCL 1090 PPM NA

525°C

<u>HOLDER</u>	<u>SAMPLE TYPE</u>	<u>FLOW RATE</u>	<u>30 MIN. WT. LOSS %</u>
PT PAN	FAB. DISC	25 CC/MIN	36.8, 36.4
PT PAN	FAB. DISC	100 CC/MIN	43.1, 43.1
AL PAN	FAB. DISC	25 CC/MIN	40.7
QUARTZ CRUCIBLE ON QUARTZ LOOP	CUT FIL.	25 CC/MIN	38.6
QUARTZ LOOP HOLDER NO PAN	FAB. DISC	25 CC/MIN	40.4

T G A O X I D A T I O N S T U D I E S

R O U N D R O B I N T E S T S

ALL FLOW RATES 25 CC/MIN

DUPONT 9900 ANALYZER

WITH QUARTZ LOOP HOLDER

525°C 30 MINUTE WEIGHT LOSS %

<u>SAMPLE NUMBER</u>	<u>QUARTZ CRUCIBLE</u>	FABRIC DISC
		8 MM <u>ON HOLDER</u>
CSA 0534	23.5	25.8
CSA 0539	18.9	24.8
CSA 0567	19.3	25.5
CCA-3 42063	19.8	24.5
CCA-3 42099	25.6	31.6
CCA-3 42352	26.3	27.8
CSA N. HOLLY 10B	100 ~10 MIN.	100 <5 MIN.
AMOCO VCX-13	16.8	17.8
WCA	NIL	NIL

T G A O X I D A T I O N S T U D I E S

R O U N D R O B I N

475°C 30 MINUTE WEIGHT LOSS %

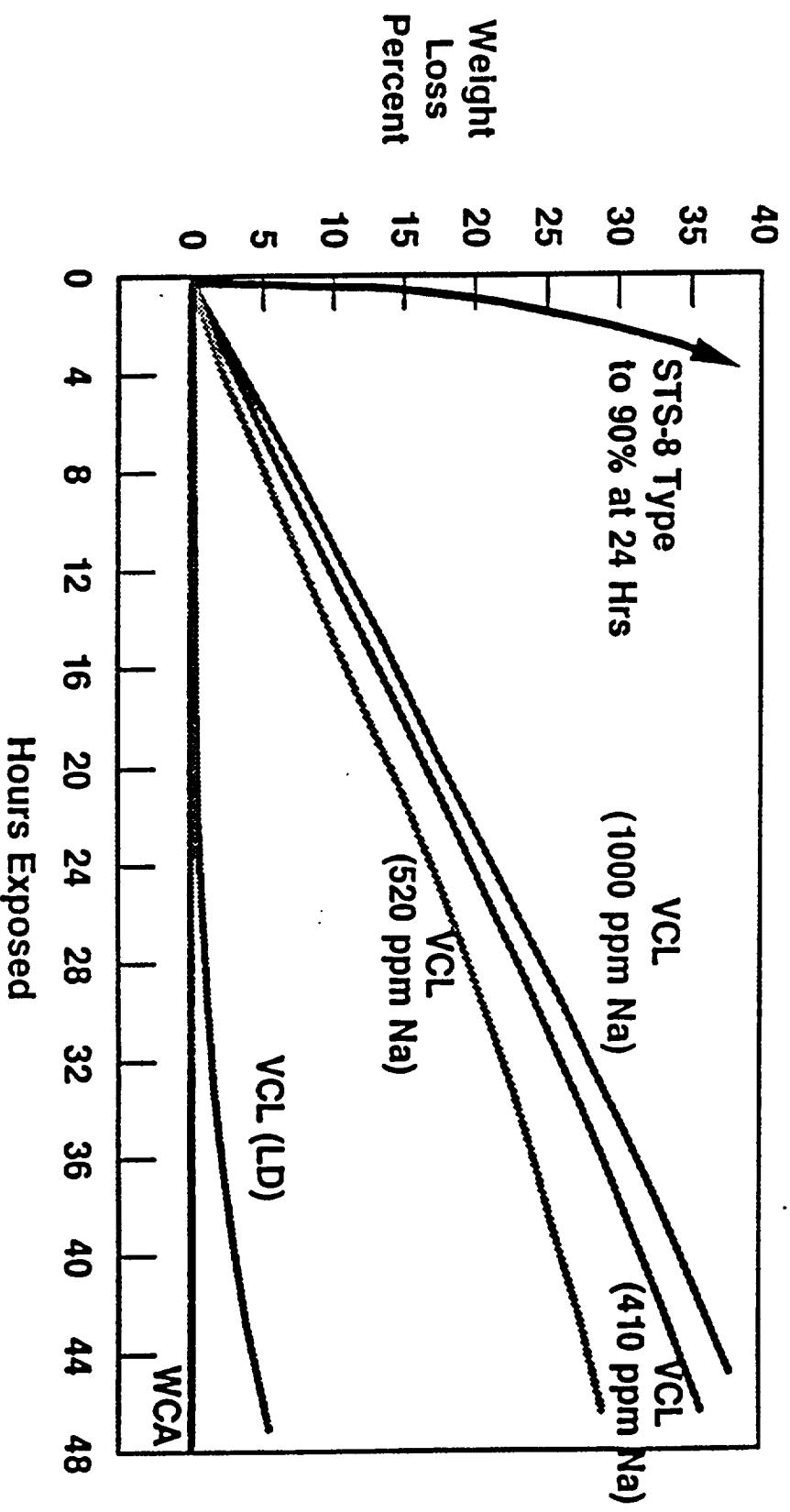
25 CC/MIN EXCEPT AS INDICATED

<u>SAMPLE</u>	<u>QUARTZ CRUCIBLE</u>	FAB DISC <u>NO PAN</u>
CSA 0534	4.6	6.1
CCA-3 42063	3.7	
CSA N.HOLLY 10B	47.8	
AMOCO VCX-13	2.6	

EFFECT OF FLOW RATE

CSA 0534	25 CC/MIN	5.2/30 MIN
	100 CC/MIN	6.2/30 MIN

OXIDATION WEIGHT LOSS AT 375°C RAYON FABRICS



June

N E C / A P P I

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WITH WCA NECESSARY (MORE THAN ONCE PER DAY)

APPENDIX D

PAT PINOLI'S PRESENTATION

TESTING CARBON FABRIC FOR OXIDATION MASS LOSS*

Dr. W. B. Hall†, L. A. Fikes‡, and P. C. Pinoli§
†Mississippi State University, Mississippi State, Mississippi
‡NASA-Marshall Space Flight Center, MSFC, Alabama
§Lockheed Research and Development Division, Palo Alto, California

ABSTRACT

Rayon based carbon fabric has been studied to assess reactivity to air oxidation/gasification. Excessive laboratory to laboratory variability of mass loss data by conventional thermal gravimetric analysis mandated a more fundamental approach to determine the sensitivity factors which influence the gasification process. Reaction activation energy and pre-exponential factor derived from the Arrhenius equation was used to assess the role of fabric firing temperature and Na catalytic action. Low temperature oxidation (400-500°C) was found to be most strongly influenced by Na catalytic action. At 400°C the oxidation rate was increased 681% by 2,240 ppm Na. The presence of water soluble Na anion significantly reduced the reaction activation energy from 34 to 21 Kcal/mole. The effect of firing temperature shifted the pre-exponential factors progressively from 2.49×10^6 to 2.63×10^3 g/g-sec after 2,500°C heat treatment. The Arrhenius temperature dependency was also used to assess laboratory to laboratory variance. Reaction rate data generated at ICI Fiberite, Tempe, Arizona, and Lockheed Research was found to deviate by 13°C, when compared at 525°C isothermal temperature.

INTRODUCTION

Rayon based carbon fabric is employed exclusively in the current ablative nozzle employed on the shuttle redesigned solid rocket motor (RSRM). The shuttle qualified commercial fabrics (VCL, CSA and CCA3) represent a class of "activated carbon" fabrics which exhibit properties not typical of other commercial carbon fiber used for structural composite applications. This paper addresses the bare fabric properties which influence air oxidation sensitivity and assess test methodology issues. The work was performed under the auspices of the NASA sponsored Solid Propulsion Integrity Program (SPIP), Nozzle Initiative Subtask 3.2.1.1 on constituent materials test methodology.

EXPERIMENTAL

A Perkin Elmer Model TGS-2 was used to measure mass loss of carbon fabrics when heated to temperature in 5 minutes and held isothermal for 30 minutes. Perkalloy magnetic transition at 596°C was used to calibrate furnace temperature. Fabric samples were prepared by cutting equal quantities of warp and fill yarns, 2-4 mm in length. Each TGA sample was pre-weighed to 4 ± 0.4 mg and packed into a 4 mm ID glass tube prior to being transferred to a quartz TGA pan. Pre-packing of each sample provided a consistent preform for transfer to the quartz pan. Bottled dry air, Linde UN-1002 with <3 ppm water, was employed with a constant purge rate of 25 ± 3 cc/minute. The programmed heating cycle employed a heating rate from 25°C to temperature of 100°C/minute, followed by an isothermal hold for 30 minutes.

DISCUSSION

The classic method to study the oxidation/gasification of carbon materials is compliance to the Arrhenius equation:

$$k = A e^{-E_a/RT}$$

where: k = specific reaction rate, sec^{-1}
 A = pre-exponential factor, sec^{-1}
 E_a = activation energy, cal/mole carbon
 R = gas constant, cal/mole - °K
 T = absolute temperature, °K

Specific reaction rates can be normalized to initial specimen weight or surface area. In this study we chose to use the specimen weight at the onset of reaching the isothermal temperature.

*This work was performed under NASA contract NASA8-37801, Solid Propulsion Integrity Program - Nozzle Initiative SUBTASK 3.2.1.1 at Lockheed R&DD, Palo Alto, California. Paper presented to JANNAF Rocket Nozzle Technology Subcommittee Meeting, NSWC, Silver Spring, MD - October 17, 1989.

Approved for public release; distribution is unlimited.

The heterogenous carbon-oxygen reaction rate of carbon fiber can be predominantly influenced by one of three zones.^{1,2,3}

Zone I relates to surface chemisorption of oxygen and concurrent desorption of CO or CO₂. Activated carbon, such as the qualified shuttle fabrics, respond strongly to this process. Zone I influence is generally predominant at low temperature (<500°C).

Zone II involves the diffusion of oxygen into the fiber micropore structure and diffusion of CO or CO₂ out of the pores. Zone II is generally predominant at moderate temperature (500-650°C).

Zone III involves the diffusion of oxygen through a stagnant gas stream of CO and CO₂ at the carbon surface. This is commonly referred to as the "reaction controlling factor", i.e., reaction products must be removed to allow carbon access to oxygen. This zone is generally most influential at higher temperature - (>650°C).

The issue of Zone III influence on TGA assessment of fiber oxidation rates at lower temperature was highly suspect due to the pan shape and variability of fiber packing. The TGA quartz pan employed in this study was about 4 mm in diameter x 1 mm deep. In order to minimize packing variability, a preform of 4±0.5 mg fibers was compacted prior to being introduced into the quartz pan. Reaction products (CO and CO₂) were not allowed to stagnate by using a high flow rate of air, 25 cc/min, directed into the quartz pan. All of the TGA runs conducted for this study were to a linear programmed heating cycle from ambient temperature to temperature in 5 minutes followed by a 30 minute isothermal hold. Isothermal temperatures were chosen to obtain measurable low rates that would preferably fall within Zone I influence.

The influence of fabric firing temperature, Na level and surface area was investigated by evaluating the reaction kinetics of 5 rayon based fabric variations. The properties of these fabrics are summarized in Table I. Experimental 10B fabric represents the effect of low firing temperature (<1300°C), high Na (2,240 ppm) and high surface area (~800 m²/g). A water washed 10B fabric was prepared by exposing a sample of as received 10B fabric to 5 sequential soakings in boiling distilled water. This operation significantly reduced Na anion level by about 40%.⁴ The CCA3 fabric represents shuttle grade fabric fired to a 1300°C range. VCX-13 fabric is a higher fired version of shuttle grade fabric-fired by Amoco -100°C above commercial VCK fabric. Unique aspects of VCX-13 vs. shuttle grade fabric is the significant reduction in measured surface area and moisture adsorption capacity: <7 m²/g and 0.7 wt% respectively. The effect of very high heat treatment is represented by commercial WCA fabric. This fabric reflects high purity, no moisture adsorption capacity and surface area close to theoretical round/solid filament (1 m²/g).

Table I. Carbon Fabric Properties

Fabric Identification	Firing Temp. °C	Fiber Density, g/cc**	Carbon Assay, wt%	Ash wt%	Na ppm	Moisture Adsorption Capacity, wt***	Surface Area, m ² /g
1. Experimental 10B	<1300	1.467	89.6	0.89	2,240/	24.4	~800
2. Experimental 10B W/W*	<1300	1.467	~89.6	~0.89	~1,000	~16	~800
3. CCA3 - Roll 42063	1300°C Range	1.482	97.6	0.2	140/170	13.6	476-923
4. VCX-13 4C7VCX 13/735	>1400	1.472	>99	0.08	25/125	0.7	<7
5. WCA	>2500	1.448	99.9	0.01	0	0.1	1

*Water Washed 5 times in distilled water.

**By Gradients Column, 60 minutes

***Weight Gain after exposure to 100% R.H. for 24 hours.

A progressive series of oxidation rates at isothermal temperature were measured on each of 5 fabric variations to assess compliance with the Arrhenius equation. Table II presents measured reaction rates with corresponding temperatures for the 5 fabric variations.

Table II. Air Oxidation Rates of Carbon Fabrics

Temperature, °C	Rates (g/g-sec x 10 ⁻⁵)				
	Exp. 10B As Received	Exp. 10B Water Washed	CCA3 (42063)	VCX-13	WCA
400	3.40	0.70			
425	5.61				
450	9.09	3.00	1.05		
475	16.5		2.37		
500	24.4	12.1	6.30	3.78	
510	32.4	16.3			
525	53.7/51.3/61.7	24.0	11.2	7.47	
535	69.1				
550	120.9	47.3	25.8	15.4	
575				30.1	1.08
600				57.0	2.32
625					3.32
650					4.93
675					9.30
700					13.6

The strong influence of firing temperature on reaction rate is evident by the need to progressively increase isothermal temperature to achieve comparable mass loss rates. The Arrhenius plots in Figure 1 however show 10B W/W, CCA3, VCX-13 and WCA all reflect a common activation energy (line slope).

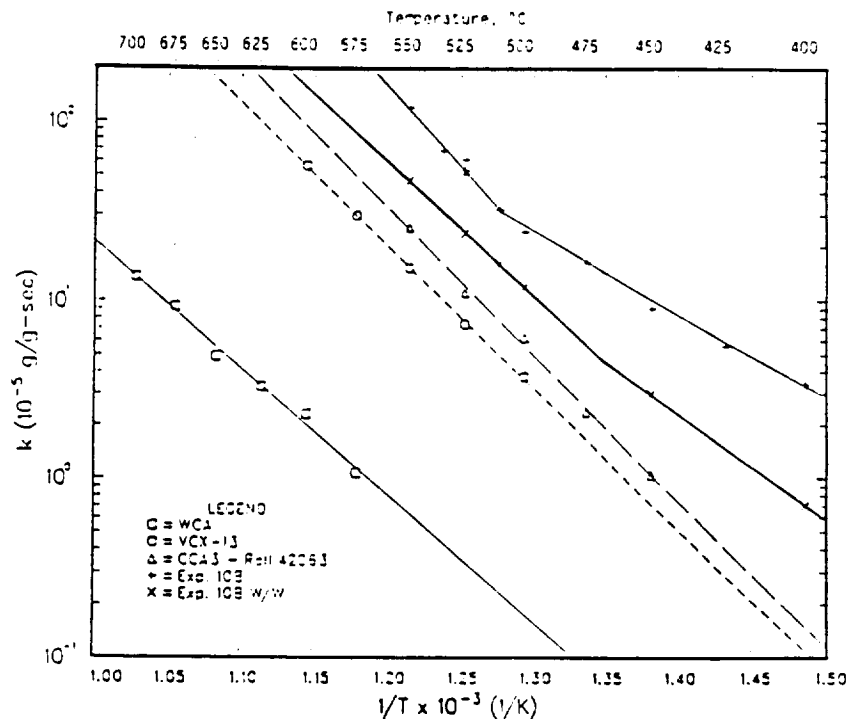


Fig. 1. Arrhenius Plots of Carbon Fabric Oxidation Response

The measured high surface areas of 10B W/W and CCA3 did not influence the oxidation reaction activation energy. Obviously Zone II oxygen diffusion into filament micropores is not an influential factor effecting the reaction activation energy. In particular, the three higher fired samples, WCA, VCX-13 and CCA3 all reflect an excellent agreement with the Arrhenius equation - temperature depending. The effect of Na catalytic action is most pronounced with as received experimental 10B fabric. The rate change at low temperature reflect a significantly lower activation energy extending up to ~500°C and transcending to a much higher energy level. Activation energy and pre-exponential factors related to the fabric samples studied are summarized in Table III.

Table III. Activation Energy and Pre-exponential Factor

Fabric Identification		Ea, Kcal/mole	A, Pre-exponential Factor
1. Experimental 10B	To 500°C	20.8±0.7	1.82 x 10 ²
	Above 500°C	40.1±2.3	5.29 x 10 ⁷
2. Experimental 10B W/W		34.2±0.5*	5.53 x 10 ⁵
3. CCA3 Roll 42063		37.6±1.3	2.49 x 10 ⁶
4. CCA3 Roll 42063**		36.2±0.7	6.42 x 10 ⁵
5. VCX-13 Roll 4C7VCX13/735		36.4±0.5	7.23 x 10 ⁵
6. WCA		32.4±1.6	2.62 x 10 ³

* 4 Data Points only, 500 to 550°C

** Data generated at ICI, Tempe, Arizona

Figure 2 compares Arrhenius plots of as received experimental 10B with 2,240 ppm Na and 10B after a water wash reduction in Na content to about 1,200 ppm. Reduction of Na level by water washing was demonstrated by previous effort.⁴ The strong influence of Na on the reaction rate of 10B as received is clearly evident from 400°C up to about 500°C. This low temperature range reflects a significantly lower activation energy of 20.8 Kcal/mole carbon. Above 500°C the activation energy is less easily defined (40.1 Kcal/mole carbon) but appears to revert to a primary Zone I influence. The water washed version of 10B reflects a small amount of Na influence as indicated by the dotted line below 475°C. The rate differences between this dotted line and the as received 10B value can be interpreted as the influence of Na on the carbon-oxygen reaction. Table IV summarizes reaction rate values and normalizes the reaction rate change to % influence of Na. The effect of Na is most pronounced at the lowest measured temperature of 400°C reflecting a 681% rate increase.

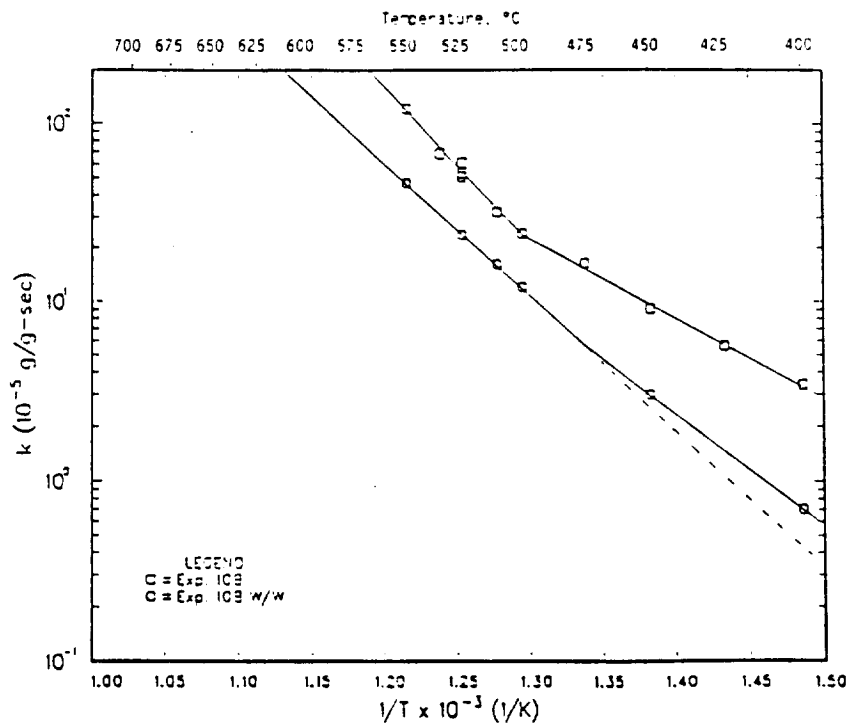


Fig. 2 Arrhenius Plots of 10B As Received vs. 10B Water Washed

Table IV. Effect of Na on Oxidation Rate of Exp. 10B Fabric

Temperature °C	A.R. Air Oxidation Rate*, g/g - sec	W.W. Air Oxidation Rate**, g/g - sec	Influence of Na, % Rate Increase
500	24.4×10^{-5}	12.1×10^{-5}	102
475	16.5×10^{-5}	5.61×10^{-5}	194
450	9.09×10^{-5}	2.54×10^{-5}	258
425	5.61×10^{-5}	1.09×10^{-5}	415
400	3.40×10^{-5}	0.435×10^{-5}	681

* As Received

** Water Washed, rates up to 475°C are extrapolated to remove Na influence

The effect of firing temperature on the reaction activation energy is minimal as indicated by a 37.6 Kcal/mole carbon value for commercial CCA3 fabric extending to a 32.4 Kcal/mole value for high fired WCA fabric. Equally important is the confirmation by the plots of close agreement with the reaction-temperature dependency of the Arrhenius equation. Lack of data scatter clearly indicates the predominant reaction kinetics in these temperature ranges is the same (Zone I). Excellent agreement of the individual run data (lack of scatter) also suggests the influence of Zone III oxygen diffusion is minimal.

The influence of fiber surface area on the reaction kinetics can be studied by analyzing measured fiber properties, TGA mass loss, and Arrhenius plots. Measured surface area (by CO₂ adsorption) for 10B, 10B W/W and conventional CCA3 reflect "activated carbon" values (476-923 m²/gm).⁴ The surface area of VCX-13 (<7 m²/gm) suggests pore closure has developed a skin/core condition; the filament skin being impermeable to CO₂ molecular intrusion and the inner core reflecting a high surface area. Fiber density analysis by gradient technique has verified the sensitivity of skin/core pore structure to oxidation.⁵ The high fired fiber, WCA reflects a surface area of 1 m²/gm - no accessible microporosity. In theory, higher fiber surface area should provide proportionally higher isothermal oxidation rates; and activation energy should be independent of surface area.

The high measured surface area fibers (10B, 10B W/W and CCA3) therefore should reflect proportionally higher oxidation rates than VCX-13 or WCA. If we assume WCA as the baseline low surface area fiber (1 m²/gm), individual oxidation rates for the other fabrics should be progressively higher in proportion to surface area. Fabric VCX-13 should reflect up to 7 times higher isothermal rates as opposed to commercial CCA3, 476 to 923 times higher. The Arrhenius plots show VCX-13 exhibits a much larger 25X increase; however CCA3 reflects a much smaller (than surface area indicates) 39X increase. This analysis indicates isothermal oxidation rates increase with higher measured fiber surface area but not in direct proportion to the measured surface area. The Arrhenius plots do show the strong influence of firing temperature on oxidation sensitivity. Unresolved however is whether high temperature heat treatment is influencing available surface area during the oxidation process and/or is reducing exposed edge plane atoms of carbon (armchair and zig zag).

The same Arrhenius plotting technique was employed to assess reproducibility of TGA data between different facilities. A series of runs on CCA3 Roll 42063 were performed at Fiberite, Tempe, Arizona, for comparison with Lockheed research data. Figure 3 compares the Arrhenius plots and shows good agreement of line slope (activation energy). Activation energy values of the runs were comparable 36-38 Kcal/mole carbon values, Ref. Table III. The line offsets suggest at 525°C the two runs reflect a potential calibration offset of 12°C. This sensitivity to calibration was further studied by using the Arrhenius equation ($E_a = 37,600$ Kcal/mole and $A = 2.49 \times 10^6$) to assess reaction rate sensitivity to isothermal temperature. The 525°C oxidation rate of shuttle grade carbon fabric will double at 549°C ($\Delta 24^\circ\text{C}$) and the 450°C oxidation rate will double at 470°C ($\Delta 20^\circ$). This defines the criticality of laboratory to laboratory calibration and indicates reducing the current mass loss test temperature from 525°C to 450°C will not significantly reduce oxidation rate sensitivity to calibration temperature.

The results of this study on cellulosic (rayon) based carbon are consistent with the behavior of other hard polymeric carbons.⁶ Similar reactivity studies on glass-like carbons developed activation energy values of 35-5 Kcal/mole carbon and the effect of heat treatment temperature is similar.^{7,8,9}

CONCLUSIONS

The oxidation behavior of rayon based carbon fabric in air was found to be in compliance with the reaction rate vs. temperature relationship of the Arrhenius equation. The reaction rate of RSRM shuttle grade carbon fabric in air can be expressed by the following equation:

$$k = 2.49 \times 10^6 e^{-37,600/RT}$$

The isothermal oxidation rates of shuttle grade fabric were found to not increase proportionally to fiber surface areas determined by CO_2 adsorption and the Dubinin-Polanyi equation. The oxidation resistance of rayon based carbon fiber was found to be strongly influenced by fabric firing temperature, with oxidation resistance increasing with firing temperature.

The oxidation sensitivity of Experimental 10B fabric is influenced by both firing temperature and Na anion level. The effect of Na catalytic action is most pronounced at low temperature and at 400°C the oxidation rate is increased by 681%. The Na catalytic effect on oxidation rate diminishes with increasing temperature and at 520°C the reaction activation energy changes from 21 to 40 Kcal/mole carbon. Removal of Na by water washing was very effective in reducing the residual Na level and the fabric oxidation rate was correspondingly reduced.

These results indicate the oxidation sensitivity of shuttle grade carbon fabric is influenced by two factors; firing temperature and Na level above ≈ 1200 ppm. Current fabric specifications monitor firing temperature by carbon assay analysis and Na content is determined by measuring the Na level in carbon fabric ash. Accurate assessment of these two factors should preclude the need for an oxidation mass loss test.

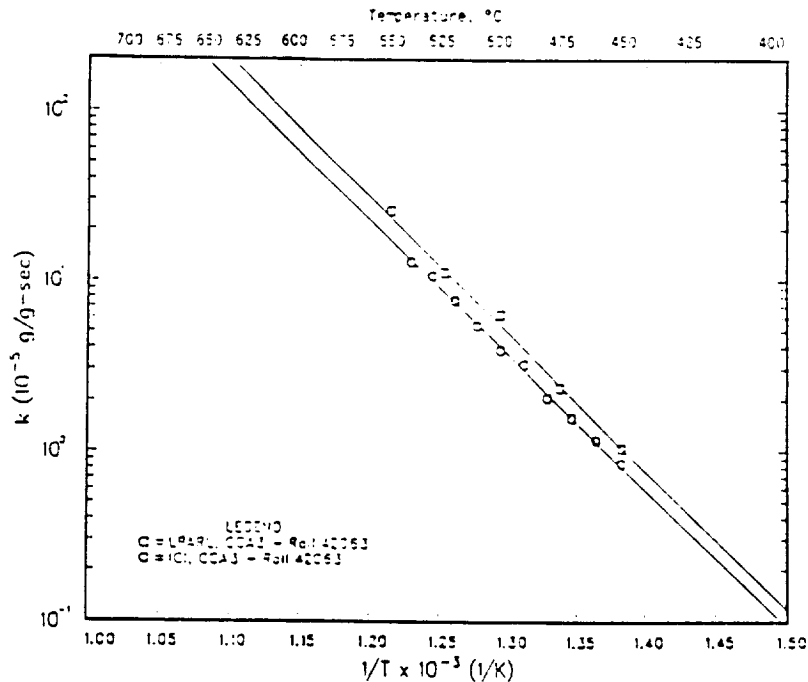


Fig. 3. Arrhenius Plots of LPARL and ICI Fiberite Generated Data

ACKNOWLEDGEMENTS

The authors thank Mr. Rob Yost of Fiberite, Tempe, Arizona, for his experimental work and technical contribution.

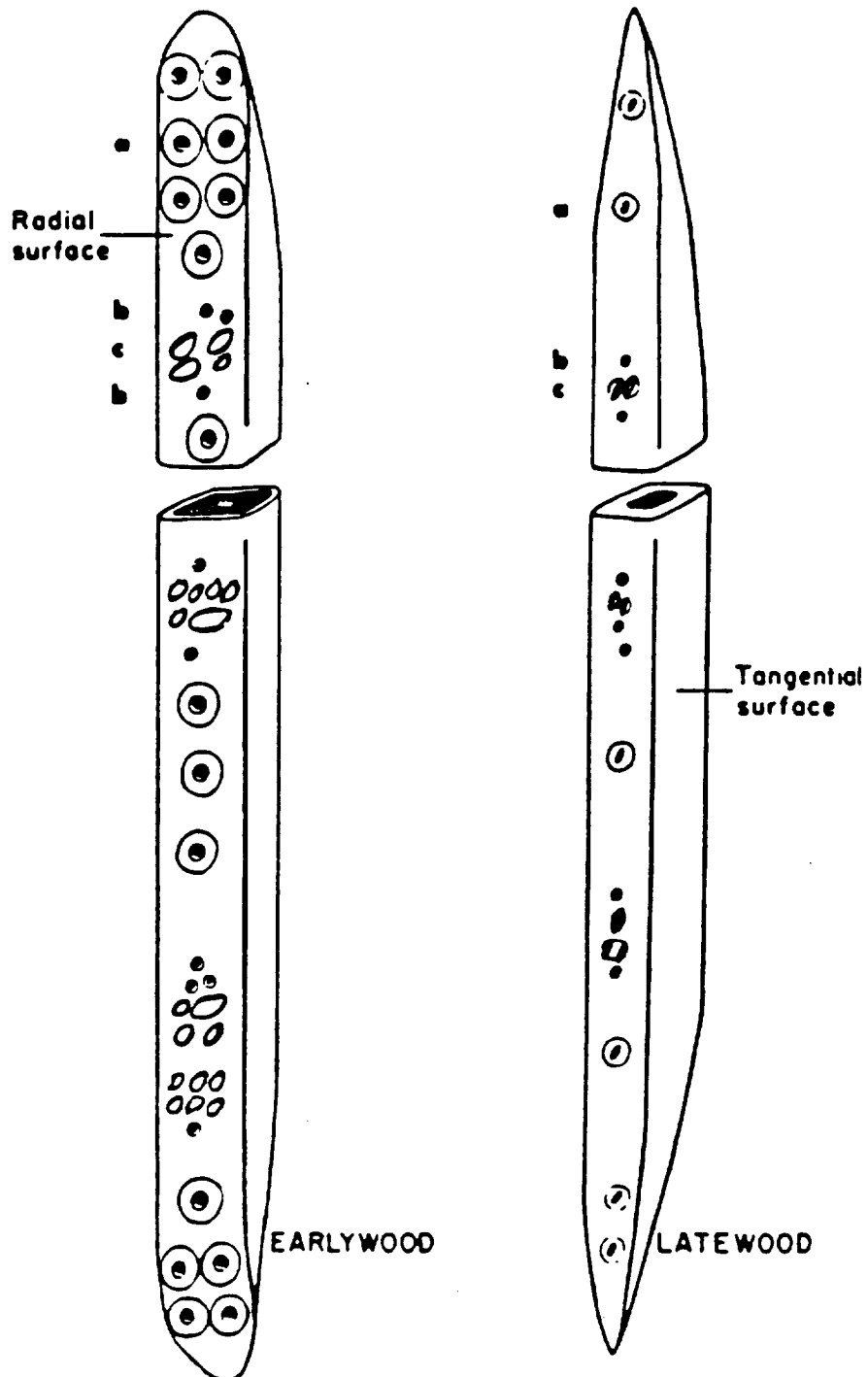
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APPENDIX E

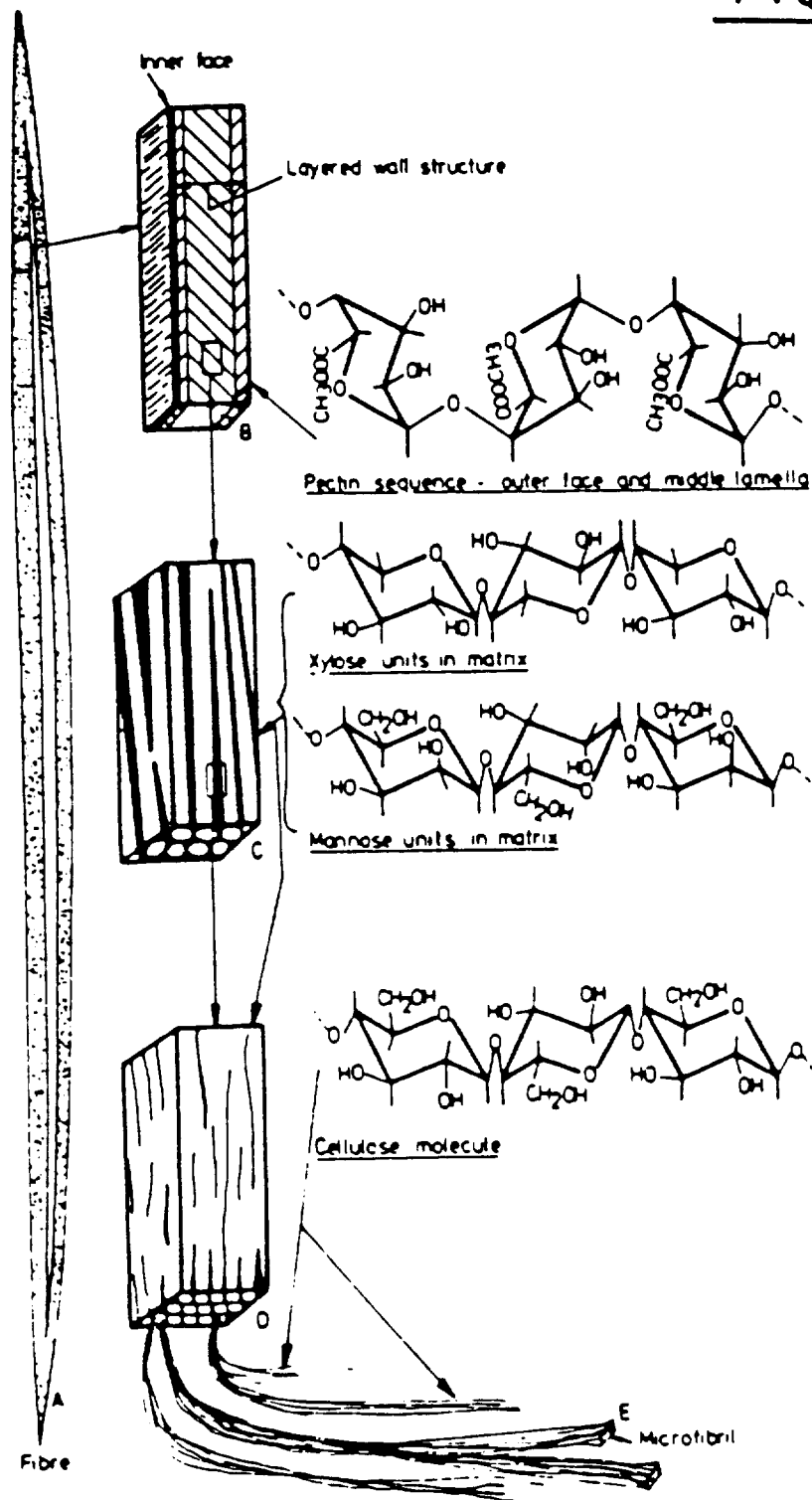
AL TURBAK'S PRESENTATION

FIG 1



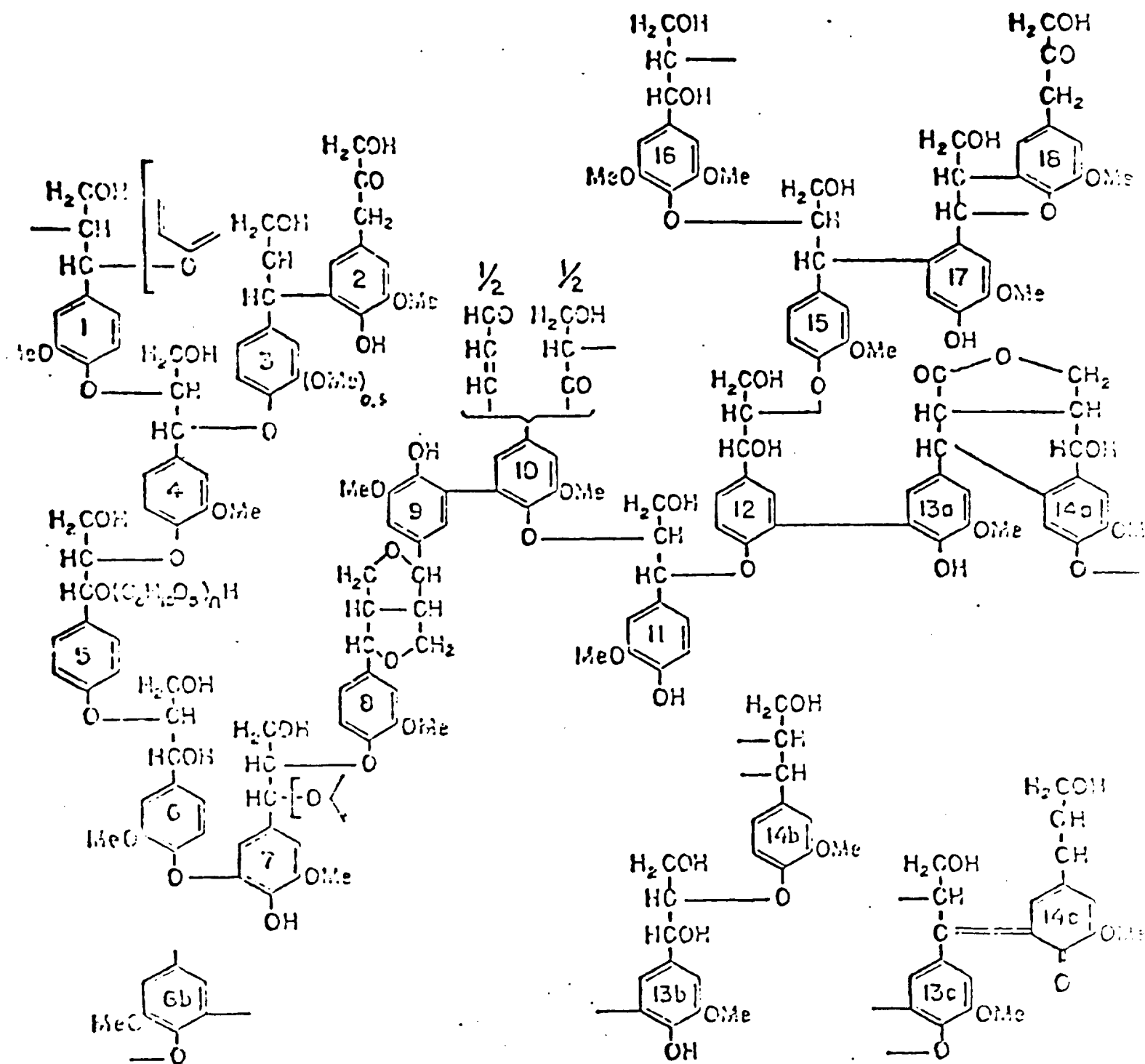
-Earlywood (left) and latewood (right) tracheids: a, intertracheid bordered pits; b, bordered pits to ray tracheids; c, pinoid pits to ray parenchyma. To simplify the drawing, tangential intertracheid pits have not been depicted. These pits are distributed along the length but are most frequent near the tracheid ends. (Drawing after Howard and Mansueti 1969.)

Fig 3



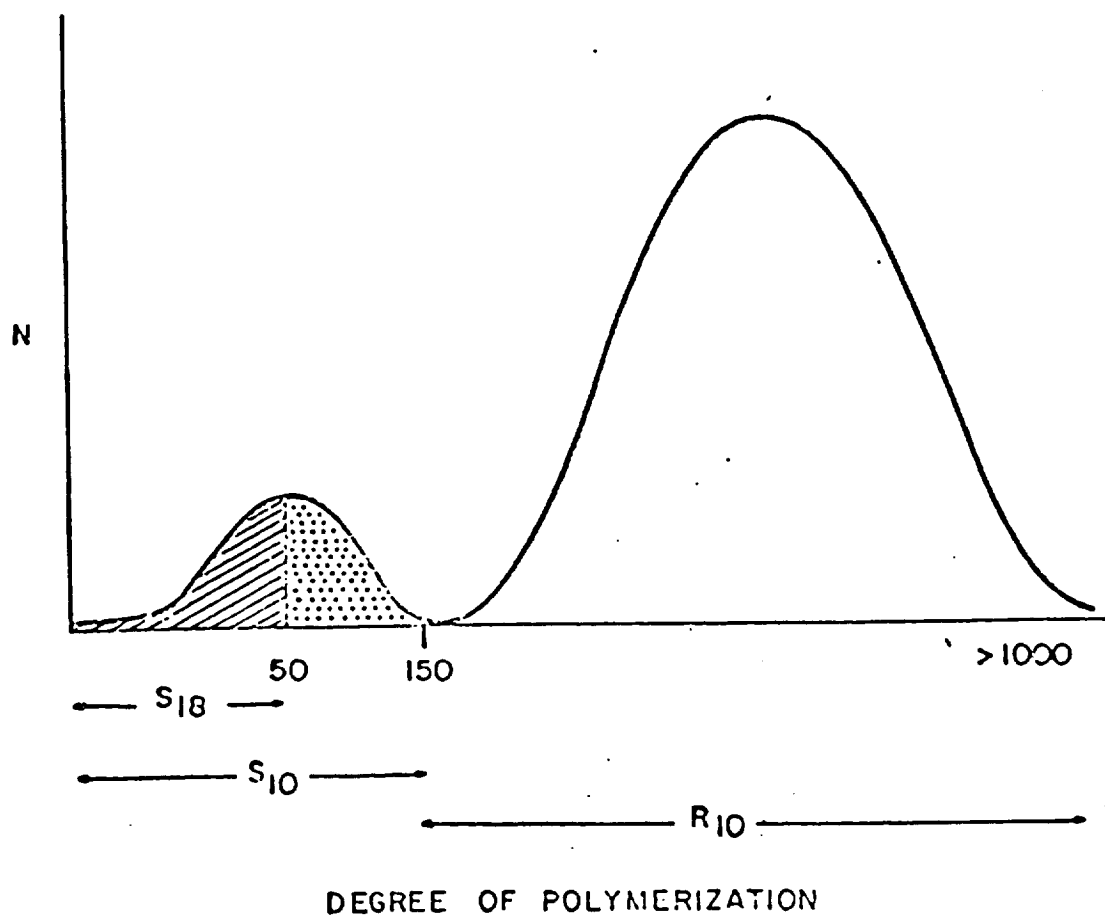
Representation of cell wall structure in a fibre cell from wood. Fibre (A) has a layered structure (B). In a fragment of the central layer of this wall (C), deposits of cellulose (white) are embedded in a matrix (black), of other polysaccharides and lignin. The cellulose deposits consist of many microfibrils (white in D) further embedded in matrix. Microfibrils consist of bundles of cellulose molecules in crystalline packing (E). Some polysaccharide components of different wall regions are shown; note that these are partial structures only (see Chapter 5). This diagram is adopted from [12].

Fig. 4



LIGNIN

FIG 5



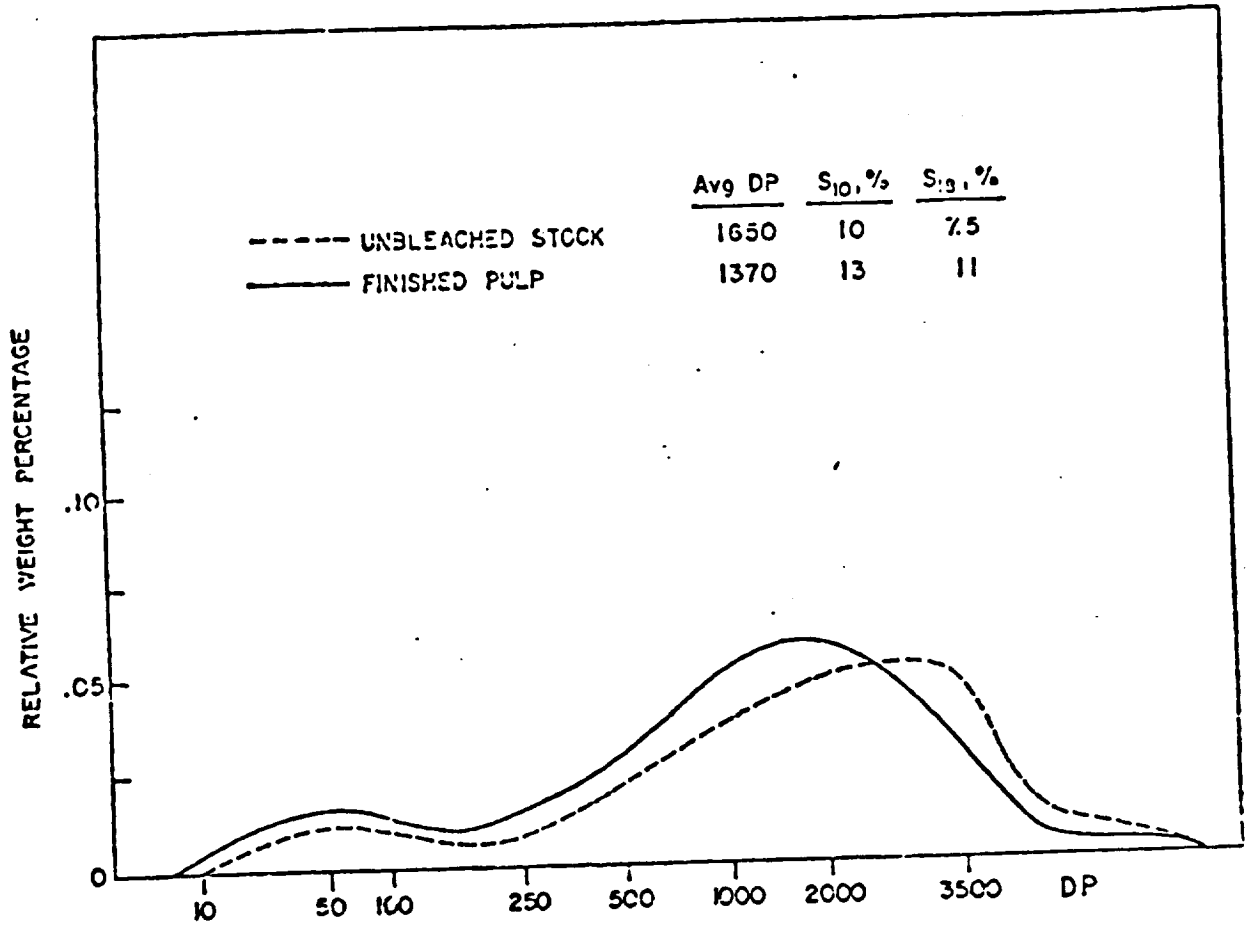
S_{10} - MAXIMUM SOLUBILITY; DISSOLVES BOTH DEGRADED CELLULOSE AND HEMICELLULOSE.

R_{10} (OR $100 - S_{10}$) IS A MEASURE OF UNDAMAGED LONG CHAIN CELLULOSE

S_{18} - REPRESENTS HEMICELLULOSES

$S_{10} - S_{18}$ - REPRESENTS DEGRADED CELLULOSE

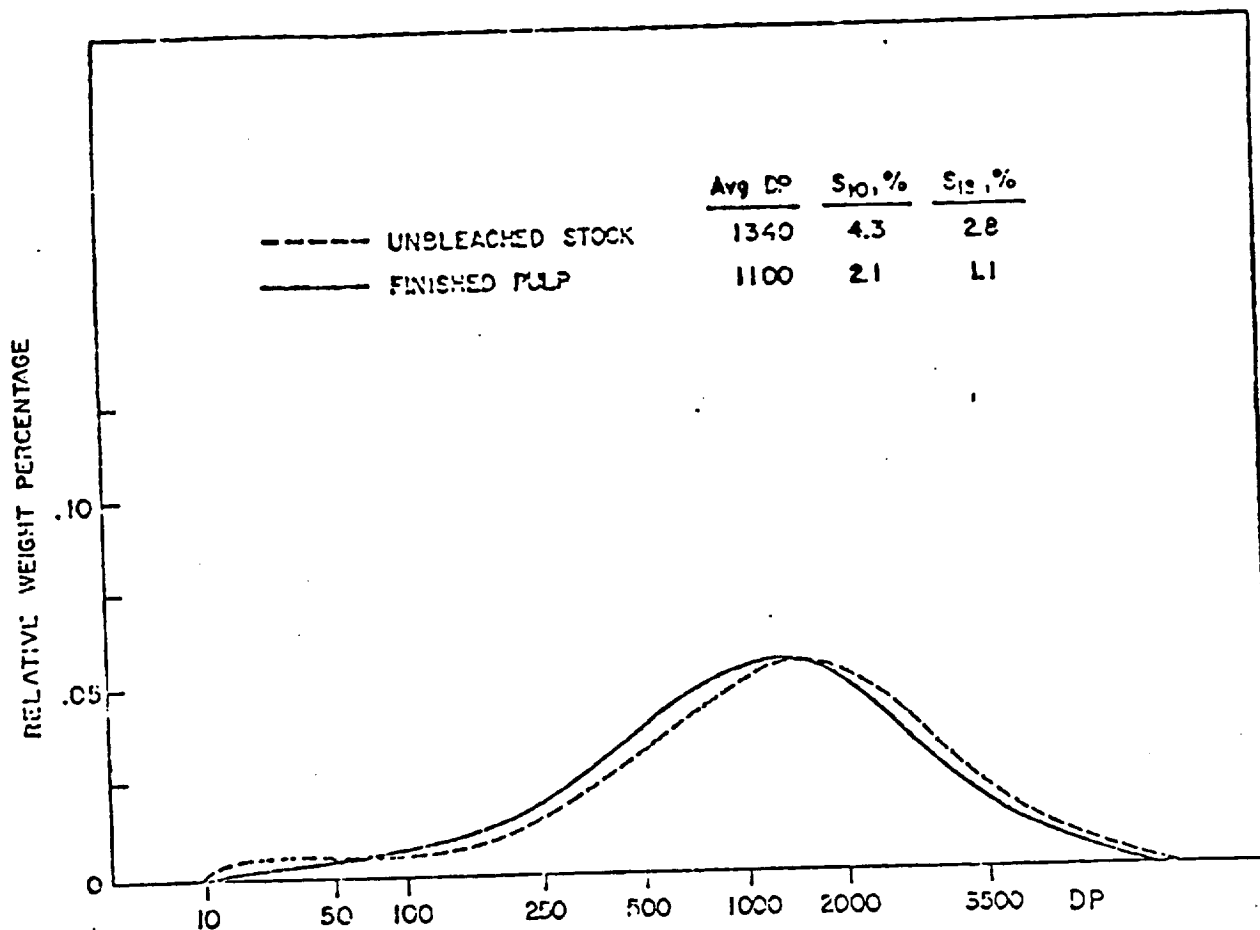
FIG 6



CONVENTIONAL KRAFT PAPER PULP

Note the broader D.P. distribution compared to sulfite paper pulp. Alkaline degradation of cellulose has caused the low D.P. "tail" of this curve to shift into the region associated with hemicelluloses.

FIG. 7

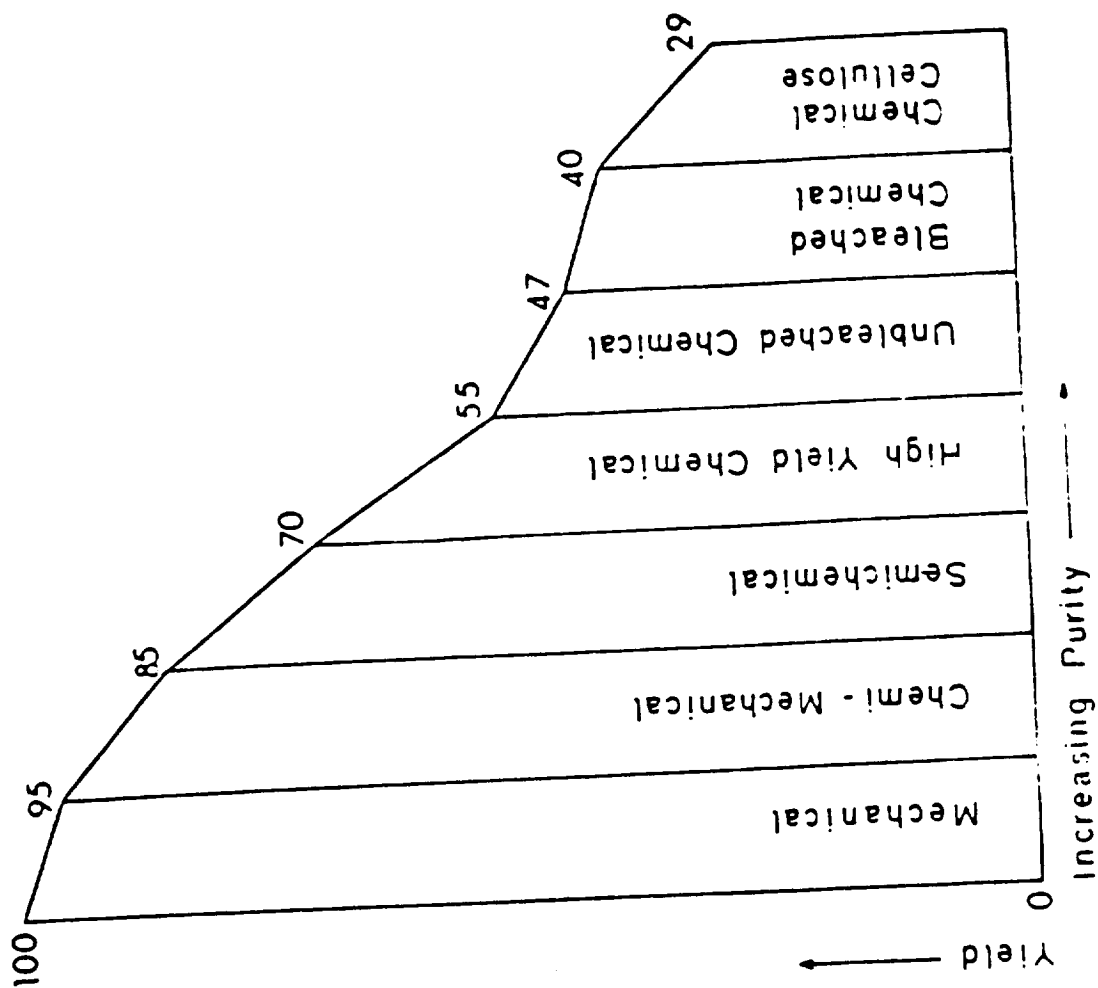


PREHYDROLYZED KRAFT DISSOLVING PULP

Hemicellulose removal in the kraft process requires an acidic treatment prior to alkaline cooking.

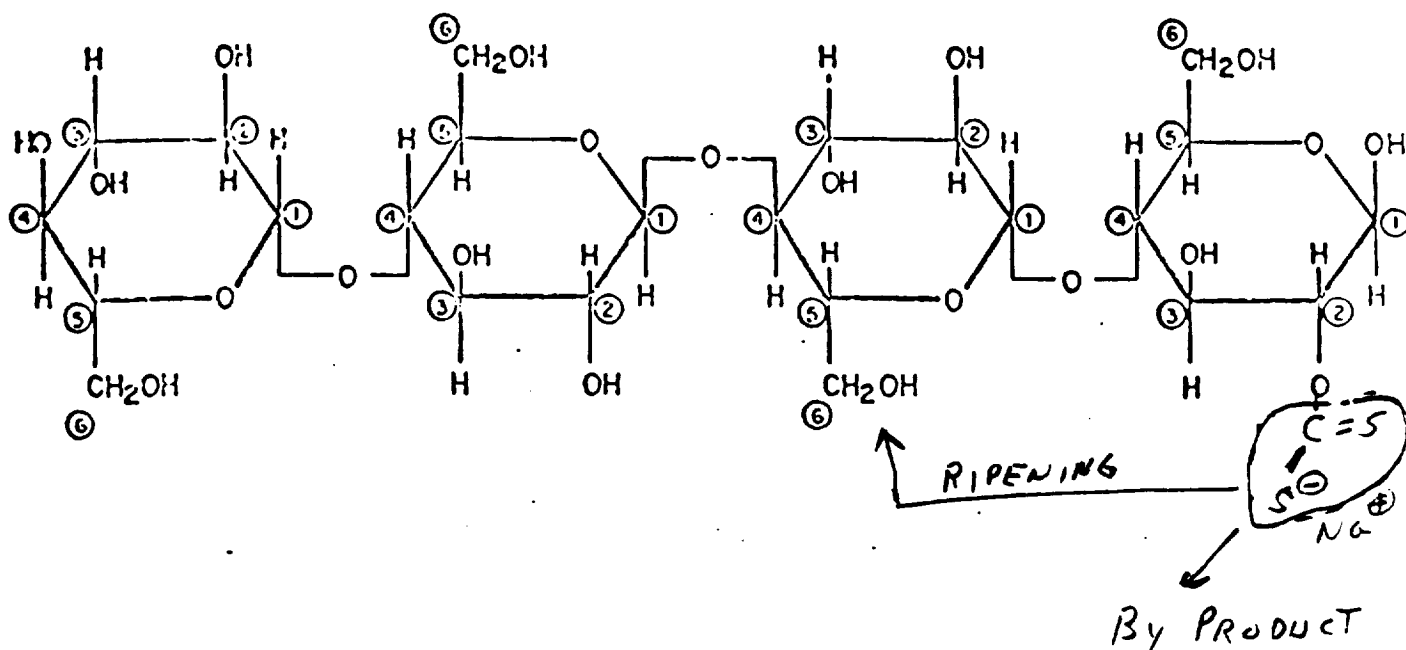
FIG 8

PULP GRADES BY YIELD AND PURITY



CELLULOSE

FIG. 9

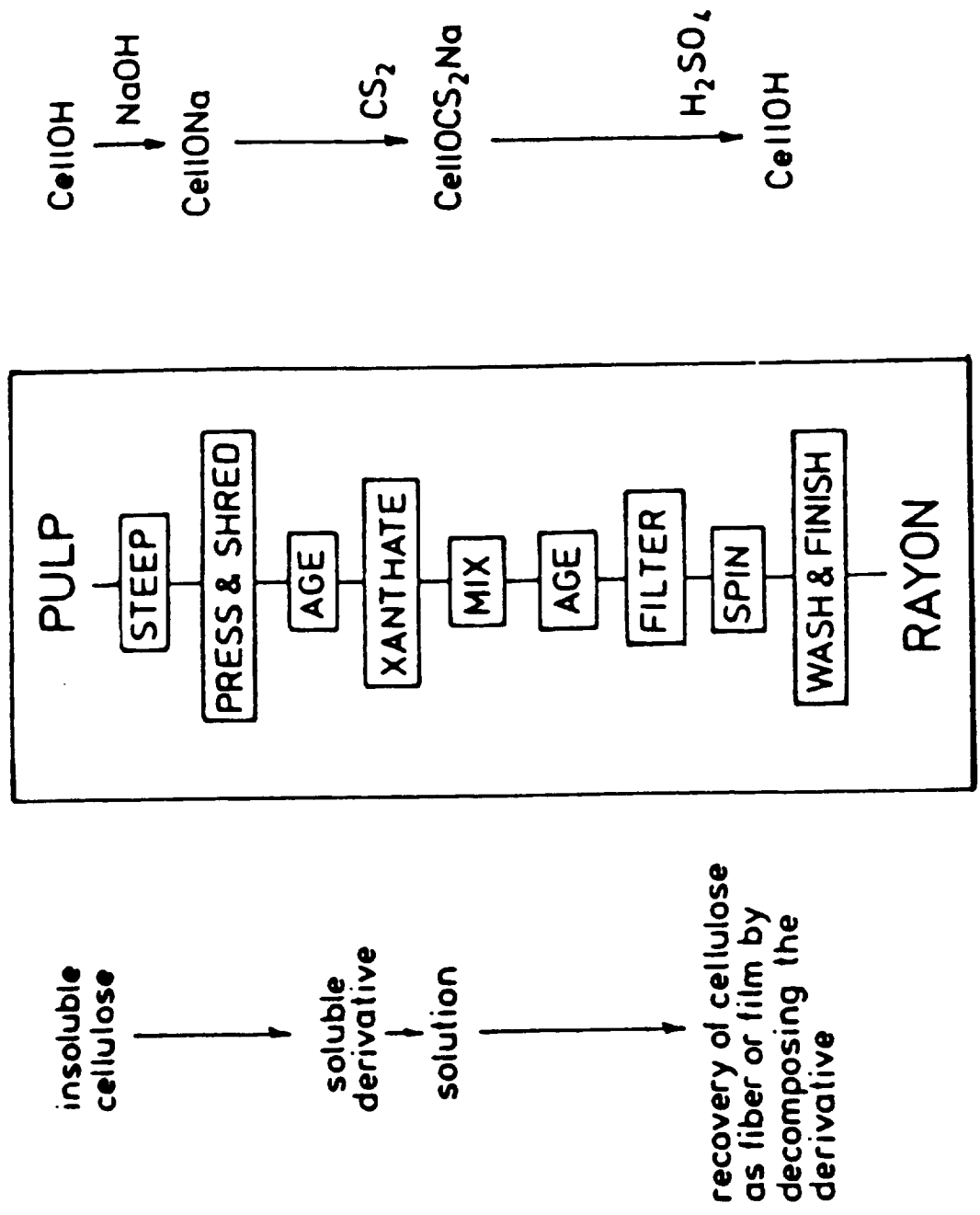


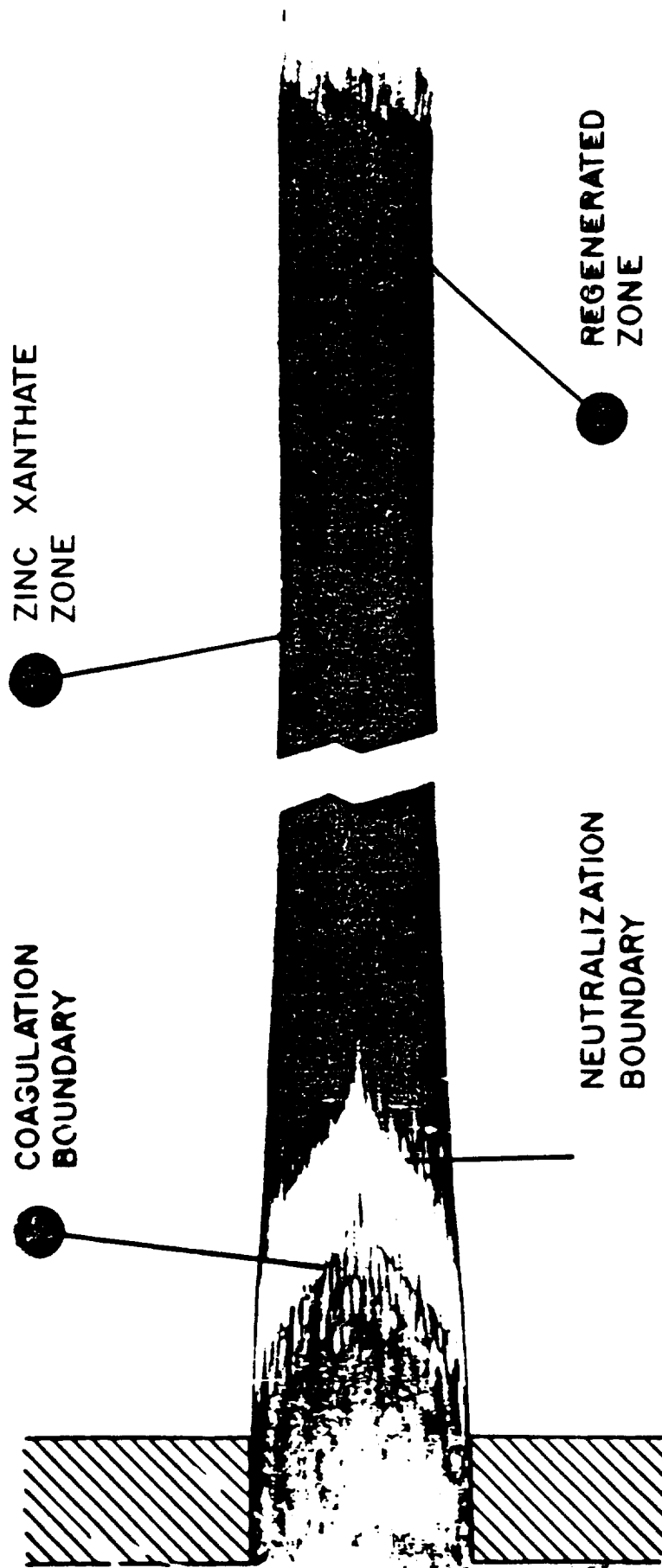
Cellulose is a long polymer composed of glucose units attached end-to-end by oxygen linkages.

<u>Material</u>	<u>Number of Glucose Units</u>
native cellulose	3,000-10,000
wood pulps	700-2,000
tire cord	400-600
cellophane	~ 300
cellulose acetates	200-400

Except for the two end units, note that each glucose unit has three hydroxyl groups, (2), (3), and (6) that are used for reaction sites for preparing cellulose derivatives.

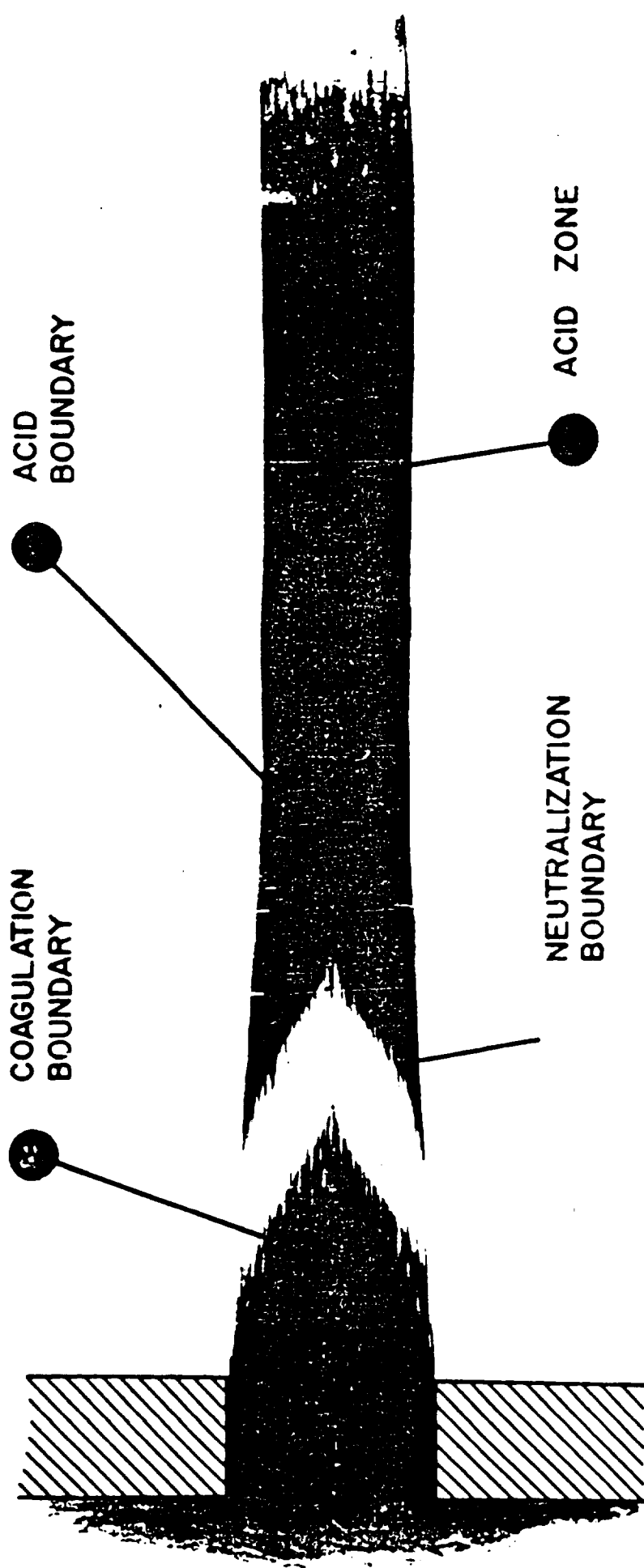
THE VISCOSE PROCESS





REGENERATION OF MODIFIED VISCOSE

FIG. 12



REGENERATION WITHOUT ZINC SALTS

TABLE I
Characteristics of Various Rayon Fibers

	Regular	LWM (IFT)*	IWM (IFT)*	IWM (IFT)*	Polynosic
Tenacity, g./den. Conditioned Wet	1.5-2.8 0.7-1.6	3.0-5.0 1.9-3.8	3.5-5.0 3.0-3.8	4.0-7.5 3.0-6.0	3.6-5.0 2.5-4.0
Elongation, % Conditioned Wet	15-30 20-35	14-25 17-30	12-17 14-20	5-10 6-11	7-11 8-15
Wet modulus, g./den.	0.12-0.25	0.12-0.25	0.5-0.7	1.8-2.5	0.9-1.1
Loop strength, g./den.	1.0-1.5	1.0-2.5	0.6-1.1	0.7-0.95	0.5-0.9
Knot strength, g./den.	0.7-1.6	1.7-2.5	0.6-1.8	1.2-2.8	1.2-2.9
Tensile strength, 1000 psi	29-46	58-90.5	60-100	80-156	60.5-120
Moisture regain, %	12-15	12.5-14.5	11-14	10-12	10-12
Fiber DP	300	300-500	350-600	600-800	550-850
Modifier	None	PEG + amine	PEG + amine	PEG, amine, HCHO	None
Stretch, %	60-120	100-120	140-150	200-400	200-300
Crystal size	Small	Small	Intermediate	Large	Large
Cross section	Skin-core	All-skin	All-skin	Layered	All-skin
Dimensional stability	Low	Low	Good	Excellent	Excellent
Caustic resistance	Low	Low	Good	Excellent	Excellent
Application	Versatile	Industrial, blends	Blends	100% c, blends	100% c, blends

* L is low, I, intermediate, and IF, high wet-modulus (WM) rayons of high tenacity (IFT).

FIG 13

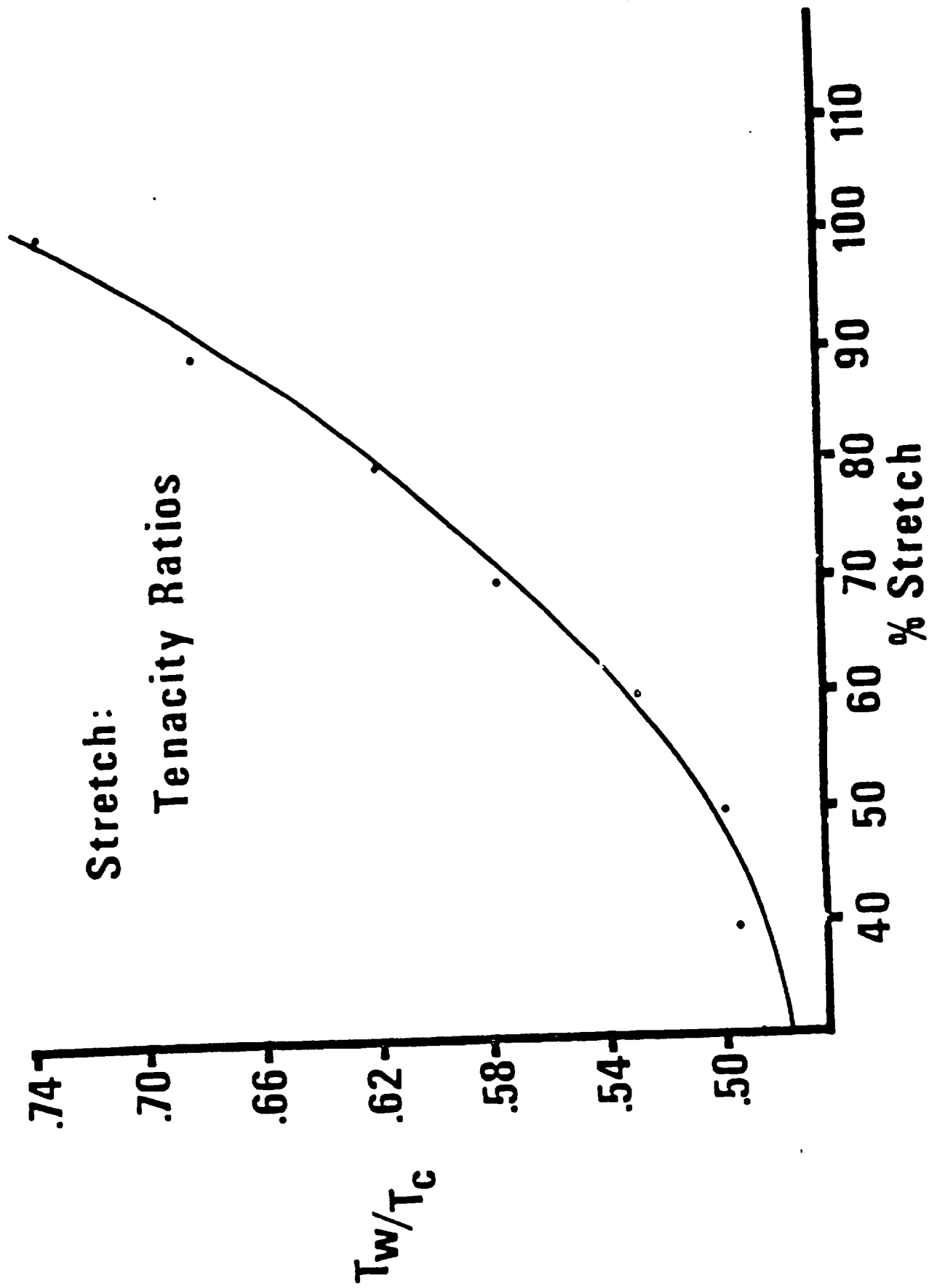
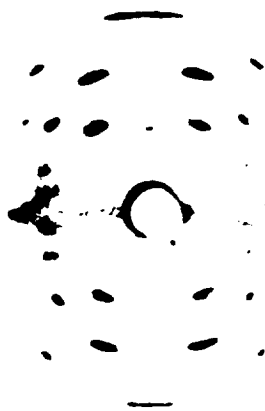


FIG 1A

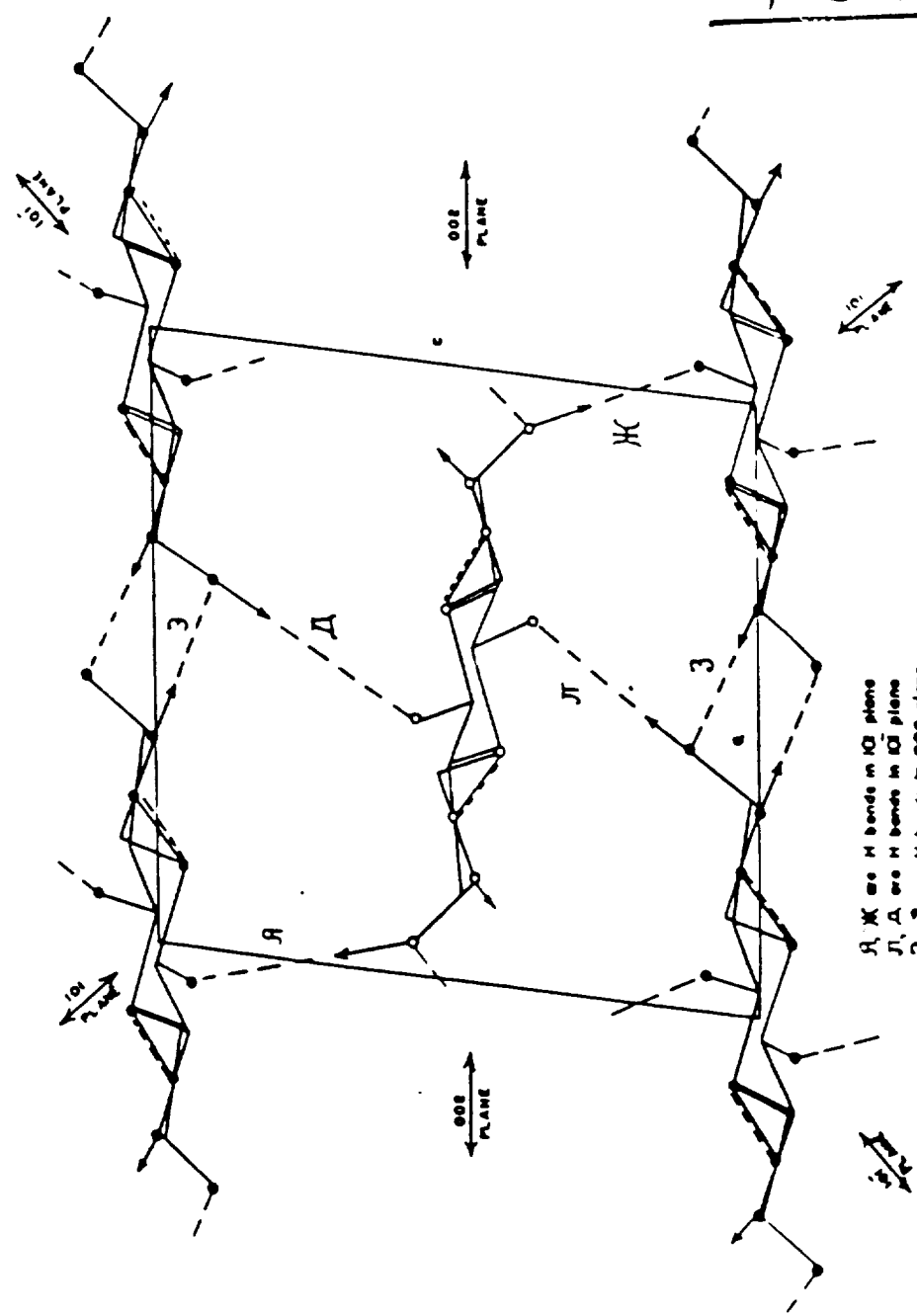


a



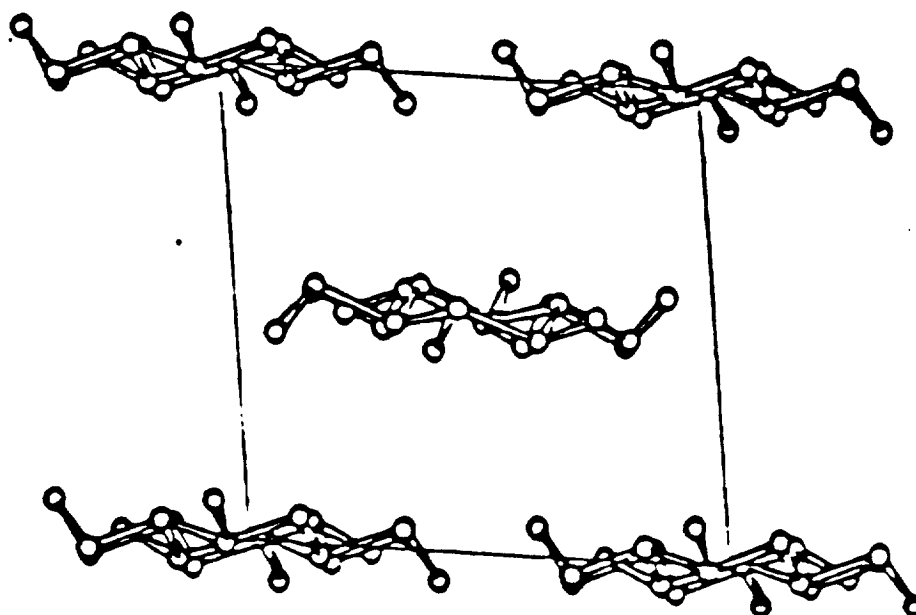
b

X-ray diffraction patterns from Fortisan,
a, and mercerized cotton, b.

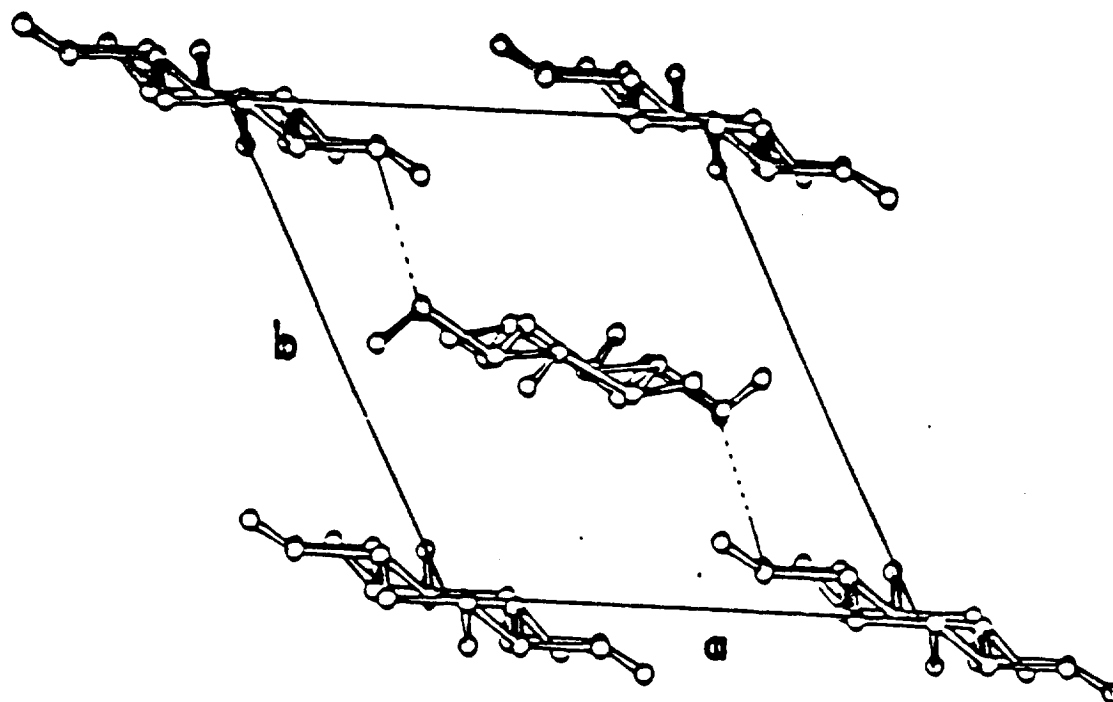


A, K are H bonds in 101 plane
 J, L are H bonds in 102 plane
 C, E are H bonds in 002 plane

FIG. 4. End view of cellulose chains in a unit cell according to Liang and Marchessault (1959)

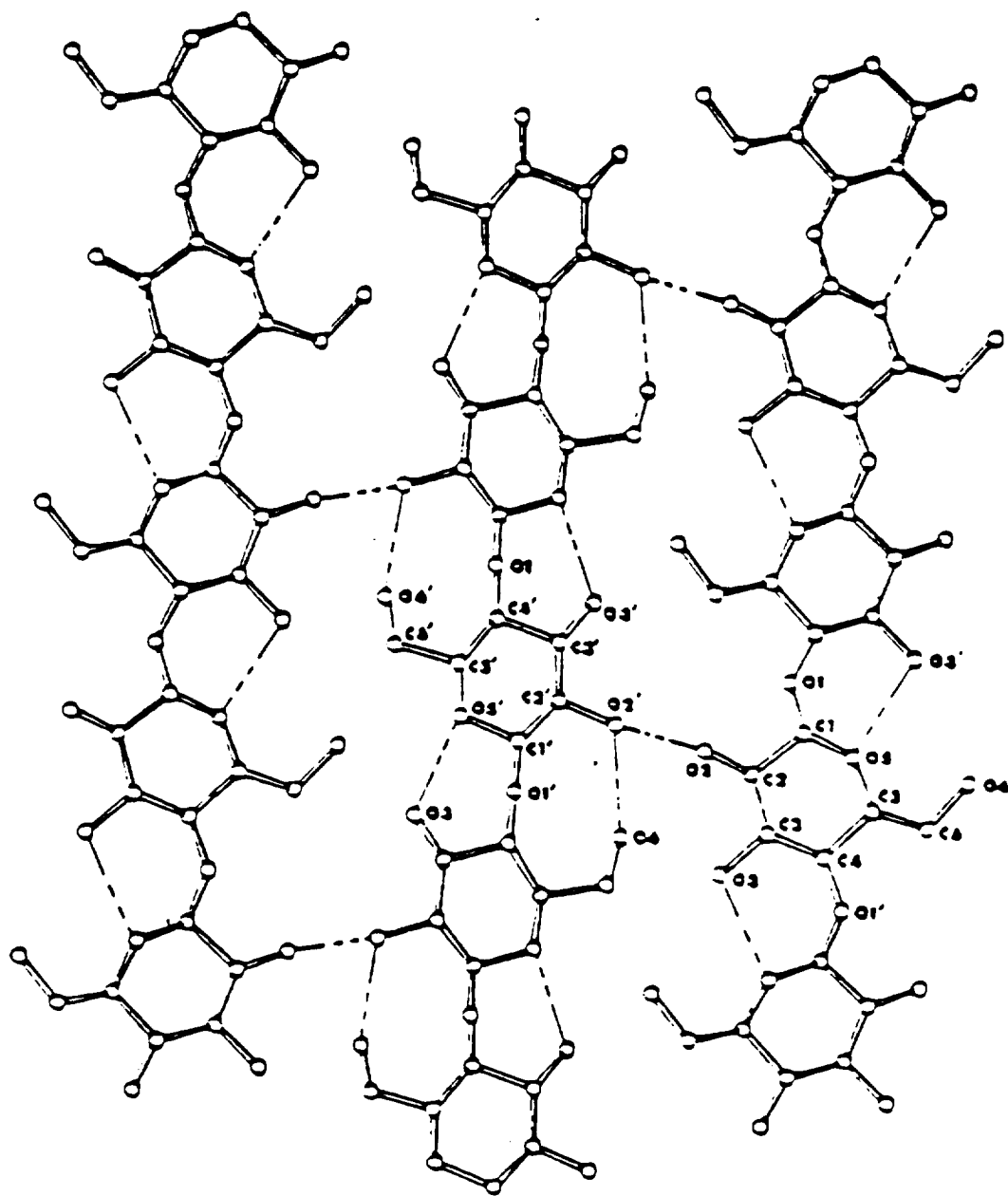


The a-b projection
of the cellulose I structure.



The a-b projection of the cellulose II
structure.

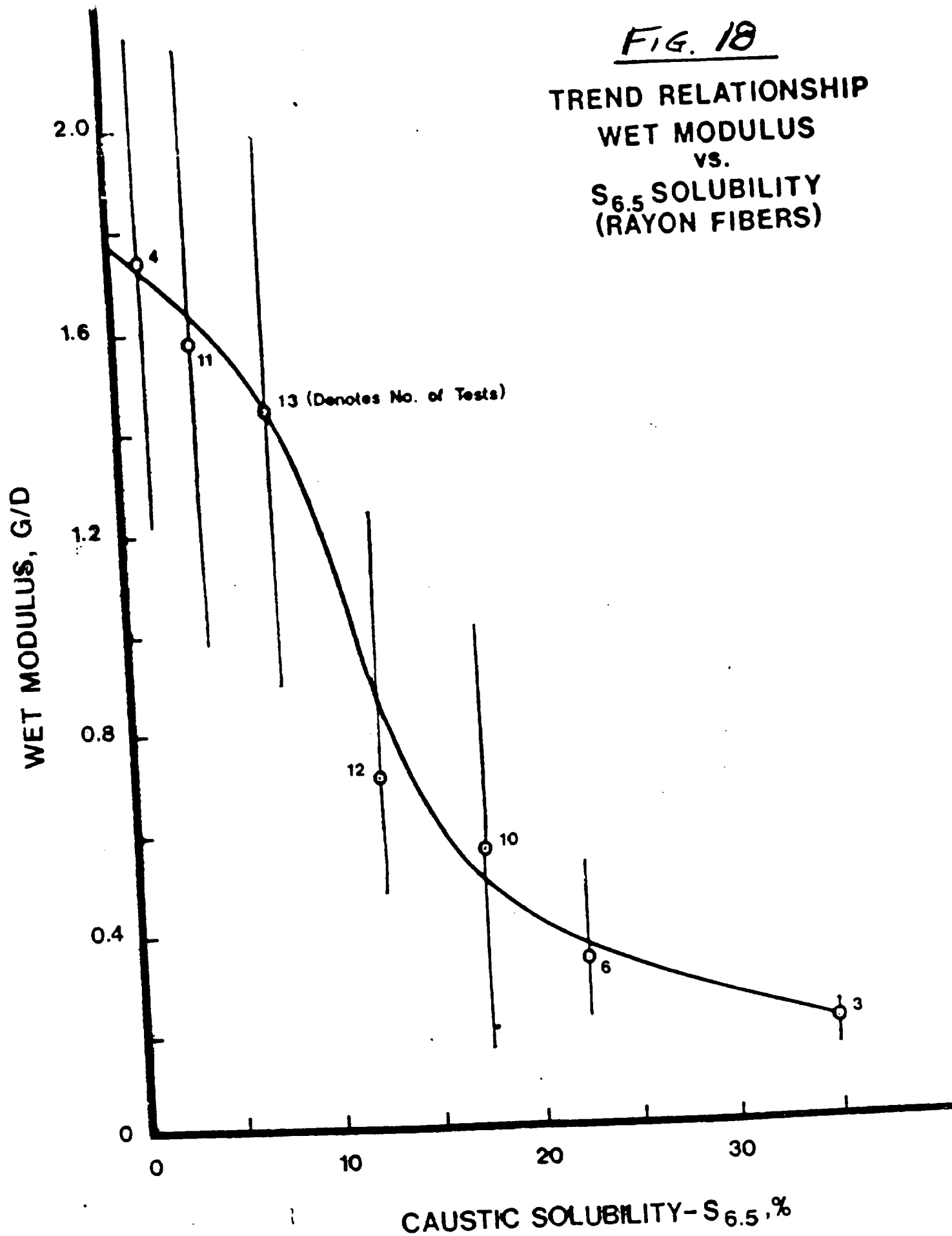
FIG 17



Intersheet hydrogen bonding along the
110 plane in cellulose II.

FIG. 18

TREND RELATIONSHIP
WET MODULUS
vs.
S_{6.5} SOLUBILITY
(RAYON FIBERS)



United States Patent (19)

Turbak et al.

[11]

4,405,549

[45]

Sep. 20, 1983

[54] ZINC-FREE PREPARATION OF RAYON FIBERS

[75] Inventors: Albin F. Turbak, Convent Station; Peter J. Hartmann, Dover, both of N.J.

[73] Assignee: International Telephone and Telegraph Corporation, New York, N.Y.

[21] Appl. No.: 283,870

[22] Filed: Jul. 13, 1981

[51] Int. Cl.³ D01F 2/06

[52] U.S. Cl. 264/188; 264/197

[58] Field of Search 264/188-197

[56] References Cited

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Primary Examiner—Jay H. Woo

Attorney, Agent, or Firm—James B. Raden; Harold J. Holt

[57]

ABSTRACT

Rayon fibers having high wet modulus, low wet elongation and low caustic solubility are prepared from an unmodified viscose spinning solution by spinning the viscose solution into a zinc-free coagulation bath containing at least 125 g/l of Na₂SO₄, at least 125 g/l of (NH₄)₂SO₄ and less than 100 g/l of H₂SO₄ while the bath is at a temperature above 40° C. The coagulated filament is then stretched in a secondary bath maintained at a temperature over 70° C.

6 Claims, No Drawings

TABLE 2

RAYON FIBER PROPERTIES FOR GRAPHITE FIBER CONVERSION

DR. A.F. TURBAK

MAY 16, 1989

<u>PROPERTY</u>	<u>VALUE</u>
D.P. (CUENE I.V. >2.0)	>300
TENSILE STRENGTH (T_c) (COND.)	3.0 ± 0.2 (g/d)
TENSILE WET/ T_c	0.4 - 0.5
ELONGATION (COND.)	<7%
ELONGATION (WET)	<10%
WET MODULUS (@ 5% TENSILE ELONGATION)	0.5 ± 0.1
REWET SWELL (CENTRIFUGE)	<60%
MOISTURE REGAIN (70°F, 65% RH)	<9.5%
CROSS SECTION (VICTORIA BLUE STAIN)	CRENULATED W/ <20% SKIN
$S_{6.5}$ @ 20°C	<8%
KNOT STRENGTH/ T_c COND.	>0.5
X-RAY CRYSTALLINITY	LOW <50%
FIBER pH	>5.8 <7.2
% SHRINK ON REWET/DRY	<3%
Na ⁺ plus K ⁺	<800 ppm TOTAL
Zn ⁺⁺	<300 ppm
SULFUR	<900 ppm
COBALT	<1 ppb
Cl ⁻	<1 ppm
ORGANIC OIL FINISH	<0.5%
POLYMERIC FINISH	<0.5%

CONDITIONED STRESS-STRAIN CURVES

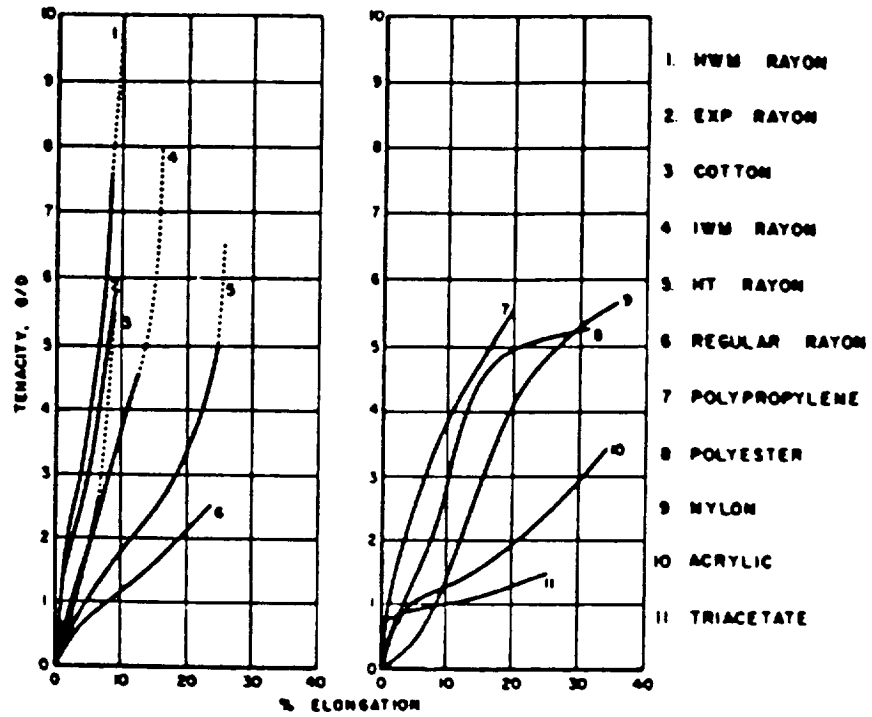


Figure 20

WET STRESS-STRAIN CURVES

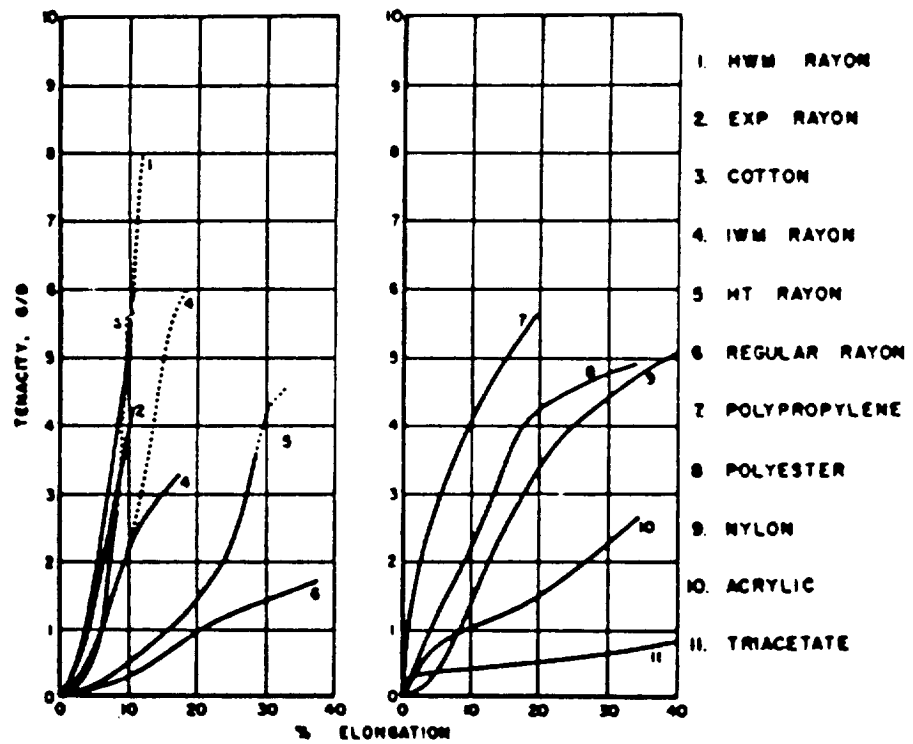


Figure 21

APPENDIX F

LOU ANN FIKE'S PRESENTATION

ORGANIZATION:		MARSHALL SPACE FLIGHT CENTER		NAME:
EH34/MSFC		ADVISORY COMMITTEE ON STANDARDIZATION OF CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS		LOU ANN FIKES
CHART NO.:				DATE:
1				MAY 16, 1989
<p>NORTH AMERICAN RAYON 2ND SOURCE PROGRAM</p> <p>NASA EFFORT</p>				

ORGANIZATION: EH34/MSFC		MARSHALL SPACE FLIGHT CENTER		NAME: LOU ANN FIKES																																				
CHART NO.: 2		NASA 2ND SOURCE RAYON EFFORT		DATE: MAY 16, 1989																																				
<p>REQUIREMENTS FOR CABONIZABLE RAYON YARN</p> <table> <tr> <td></td> <td><u>1650/720</u></td> <td><u>1100/490</u></td> </tr> <tr> <td>ASH (%)</td> <td>0.45 MAX</td> <td>0.45 MAX</td> </tr> <tr> <td>SULFUR (%)</td> <td>0.25 MAX</td> <td>0.25 MAX</td> </tr> <tr> <td>ZINC (%)</td> <td>0.07 MAX</td> <td>0.07 MAX</td> </tr> <tr> <td>PH</td> <td>5.0 - 8.0</td> <td>5.0 - 8.0</td> </tr> <tr> <td>FINISH (%)</td> <td>0.2 - 1.0</td> <td>0.2 - 1.0</td> </tr> <tr> <td>TWIST (TURNS/INCH)</td> <td>1.6 - 2.4</td> <td>1.4 - 2.2</td> </tr> <tr> <td>BREAK STRENGTH (LBS.)</td> <td>10.3 - 13.5</td> <td>7.0 - 9.6</td> </tr> <tr> <td>ELONGATION (%)</td> <td>5.5 - 9.5</td> <td>5.4 - 9.4</td> </tr> <tr> <td>MOISTURE (%)</td> <td>13.0 MAX</td> <td>13.0 MAX</td> </tr> <tr> <td>DENIER</td> <td>1590 - 1710</td> <td>1060 - 1140</td> </tr> <tr> <td>SHRINKAGE (%)</td> <td>2.9 - 4.7</td> <td>2.6 - 4.6</td> </tr> </table>						<u>1650/720</u>	<u>1100/490</u>	ASH (%)	0.45 MAX	0.45 MAX	SULFUR (%)	0.25 MAX	0.25 MAX	ZINC (%)	0.07 MAX	0.07 MAX	PH	5.0 - 8.0	5.0 - 8.0	FINISH (%)	0.2 - 1.0	0.2 - 1.0	TWIST (TURNS/INCH)	1.6 - 2.4	1.4 - 2.2	BREAK STRENGTH (LBS.)	10.3 - 13.5	7.0 - 9.6	ELONGATION (%)	5.5 - 9.5	5.4 - 9.4	MOISTURE (%)	13.0 MAX	13.0 MAX	DENIER	1590 - 1710	1060 - 1140	SHRINKAGE (%)	2.9 - 4.7	2.6 - 4.6
	<u>1650/720</u>	<u>1100/490</u>																																						
ASH (%)	0.45 MAX	0.45 MAX																																						
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MOISTURE (%)	13.0 MAX	13.0 MAX																																						
DENIER	1590 - 1710	1060 - 1140																																						
SHRINKAGE (%)	2.9 - 4.7	2.6 - 4.6																																						

ORGANIZATION: EH34/MSFC		MARSHALL SPACE FLIGHT CENTER		NAME: LOU ANN FIKES
CHART NO.: 3		NASA 2ND SOURCE RAYON EFFORT		DATE: MAY 16, 1989

NARC - CARBNIZABLE RAYON DEVELOPMENT (AS OF MARCH 31, 1989) -

- o NARC HAS MADE 18 SAMPLES VARYING THE SPIN BATH AND SPINNING MACHINE PARAMETERS BUT NOT THE CHEMISTRY OF THE VISCOSE
- o NONE OF THE 18 SAMPLES MEET ALL THE REQUIREMENT OF THE SPECIFICATION
- o CRITICAL REQUIREMENTS DIFFICULT TO HIT CONCURRENTLY ARE:
 - 1. CONDITIONED BREAK STRENGTH
 - 2. CONDITIONED ELONGATION
 - 3. SHRINKAGE
- o 3 OF THE 18 FORMULATIONS WERE SELECTED AS POTENTIAL FOR RE-ENTRY VEHICLE AND PROPULSION (D-5) PREPGREG AND 5,500 POUNDS OF EACH WERE MADE

ORGANIZATION: EH34/MSFC	MARSHALL SPACE FLIGHT CENTER		NAME: LOU ANN FIKES
CHART NO.: 4	NASA 2ND SOURCE RAYON EFFORT		DATE: MAY 16, 1989

NARC RAYON YARN TESTS
PRODUCTION 6B COMPARISON

VARIABLE	SPEC	AVTEX AVG	TRIAL 6B AVG	PRODUCTION 6B AVG
DENIER	1590 - 1710	1666	1652	1656
STRENGTH	10.3 - 13.5	12.6	13.0	13.3
ELONGATION	5.5 - 9.5	8.4	11.3	10.5
TWIST	1.6 - 2.4	1.9	2.2	1.7
SHRINKAGE	2.9 - 4.7	4.2	5.4	5.7
MOISTURE	13.0 MAX	8.9	12.0	11.4
FINISH	0.2 - 1.0	0.42	0.3	0.7
PH	5.0 - 8.0	5.5	8.7	7.3
ASH	0.45 MAX	0.30	0.35	0.29
ZINC	0.07 MAX	0.03	0.05	0.05
SULFUR	0.25 MAX	0.14	0.09	0.11

TRAIL AND PRODUCTION MATERIAL CLOSE TOGETHER, BUT NARC HAS REFUSED TO
MAKE THIS MATERIAL AS A PRODUCTION MATERIAL

○ = DOES NOT MEET REQUIREMENT

◇ = DIFFERENCE BETWEEN TRIAL AND PRODUCTION

NARC STOPPED PRODUCING THIS BECAUSE IT COULD NOT BE MADE CONSISTENTLY

ORGANIZATION: <div style="border: 1px solid black; padding: 2px; text-align: center;">EH34/MSFC</div>	MARSHALL SPACE FLIGHT CENTER <div style="border: 1px solid black; padding: 2px; text-align: center;">NASA 2ND SOURCE RAYON EFFORT</div>	NAME: <div style="border: 1px solid black; padding: 2px; text-align: center;">LOU ANN FIKES</div>
CHART NO.: <div style="border: 1px solid black; padding: 2px; text-align: center;">5</div>	DATE: <div style="border: 1px solid black; padding: 2px; text-align: center;">MAY 16, 1989</div>	

NARC RAYON YARN TESTS
PRODUCTION 12B COMPARISON

VARIABLE	SPEC	AVTEX AVG	TRIAL 12B AVG	PRODUCTION 12B AVG
DENIER	1590 - 1710	1666	1639	1657
STRENGTH	10.3 - 13.5	12.6	12.8	12.6
ELONGATION	5.5 - 9.5	8.4	(12.6) ◇	(11.2)
TWIST	1.6 - 2.4	1.9	1.9	1.8
SHRINKAGE	2.9 - 4.7	4.2	(5.4)	(5.6)
MOISTURE	13.0 MAX	8.9	11.4	10.75
FINISH	0.2 - 1.0	0.42	(1.4) ◇	0.32
PH	5.0 - 8.0	5.5	7.5	6.75
ASH	0.45 MAX	0.30	0.27	0.24
ZINC	0.07 MAX	0.03	0.44	.047
SULFUR	0.25 MAX	0.14	0.14	.085

= DOES NOT MEET REQUIREMENT
 = DIFFERENCE BETWEEN TRIAL AND PRODUCTION

ORGANIZATION: EH34/MSFC	MARSHALL SPACE FLIGHT CENTER		NAME: LOU ANN FIKES
CHART NO.: 6	NASA 2ND SOURCE RAYON EFFORT		DATE: MAY 16, 1989

**NARC RAYON YARN TESTS
PRODUCTION 13A COMPARISON**

<u>VARIABLE</u>	<u>SPEC</u>	<u>AVTEX AVG</u>	<u>TRIAL 13A AVG</u>	<u>PRODUCTION 13A AVG</u>
DENIER	1590 - 1710	1666	1664	1648
STRENGTH	10.3 - 13.5	12.6	12.4	11.8
ELONGATION	5.5 - 9.5	8.4	<u>17.2</u> ◇	<u>13.6</u>
TWIST	1.6 - 2.4	1.9	2.0	1.8
SHRINKAGE	2.9 - 4.7	4.2	<u>5.9</u>	<u>5.7</u>
MOISTURE	13.0 MAX	8.9	11.6	11.7
FINISH	0.2 - 1.0	0.42	<u>2.0</u>	<u>1.6</u>
PH	5.0 - 8.0	5.5	6.9	7.3
ASH	0.45 MAX	0.30	0.30	0.24
ZINC	0.07 MAX	0.03	0.05	0.04
SULFUR	0.25 MAX	0.14	0.13	.011

○ = DOES NOT MEET REQUIREMENT

◇ = DIFFERENCE BETWEEN TRIAL AND PRODUCTION

ORGANIZATION: EH34/MSFC		MARSHALL SPACE FLIGHT CENTER		NAME: LOU ANN FIKES	
CHART NO.: 7		NASA 2ND SOURCE RAYON EFFORT		DATE: MAY 16, 1989	

CHARACTERISTICS OF VARIOUS RAYONS		NARC PRODUCTION RUNS				
REQUIRED		AVTEX	(HT)	13A	12B	6B
*STRENGTH [LBS]	10.3/13.5	12.6		11.8	12.6	13.3
*ELONGATION [%]	5.5 9.5	8.4		13.6	11.2	10.5
MOISTURE [%]	13.0 MAX	8.9		11.7	10.8	11.4
DP	(N/A)	325		425	425	425
SHRINKAGE [%]	2.7/ 4.7	4.2		5.7	5.6	5.7
S6.5 [%]	8.0	8.0		8.5	8.5	12.0
MODIFIERS	(NONE)	NONE		NONE	NONE	NONE
SKIN/CORE	THICK SKIN			T. SKIN	(N/A)	(N/A)
COPPER NUMBER	0.62			0.35	0.37	0.37
SULFATE [%]	(NOT DETECTED)			0.039	0.041	0.032
*CONDITIONED (HT) = HIGH TENACITY						

ORGANIZATION: EH34/MSFC		MARSHALL SPACE FLIGHT CENTER		NAME: LOU ANN FIKES
CHART NO.: 8		NASA 2ND SOURCE RAYON EFFORT		DATE: MAY 16, 1989

O ON APRIL 10, 1989 NASA GAVE NARC THE AUTHORITY TO PROCEED WITH FACILITY MODIFICATIONS TO DEVELOP A LINE DEDICATED TO NASA

- DEVELOP AN AVTEX "CLONE"
- 5 WEEKS TO COMPLETE FACILITY MODS
 - O FINISH SYSTEM
 - O VISCOSE SYSTEM
 - O SPIN BATH SYSTEM
 - O INSTRUMENTATION
- EXPERIMENTAL DESIGN INCLUDES 16 RUNS

ORGANIZATION: EH34/MSFC		MARSHALL SPACE FLIGHT CENTER NASA 2ND SOURCE RAYON EFFORT	NAME: LOU ANN FIKES
CHART NO.: 9			DATE: MAY 16, 1989

VISCOSE PARAMETERS FOR NARC TO VARY IN THE EXPERIMENTAL DESIGN -

- 1. VISCOSITY
- 2. CAUSTIC CONTENT
- 3. CELLULOSE CONTENT
- 4. CS2 CONTENT

ORGANIZATION: EH34/MSFC		MARSHALL SPACE FLIGHT CENTER NASA 2ND SOURCE RAYON EFFORT		NAME: LOU ANN FIKES
CHART NO.: 10		DATE: MAY 16, 1989		
<p style="text-align: center;"><u>NARC SCHEDULE</u></p> <p>0 SPINNING BEGINS MAY 17</p> <p>0 2 VARIATIONS PLANNED FOR THE FIRST WEEK</p> <p>0 3 VARIATIONS PER WEEK AFTER THE FIRST WEEK</p> <p>0 PLANS INCLUDE 16 VARIATIONS</p> <p>0 CRITICAL REQUIRED TESTING TAKES 3 DAYS TO COMPLETE</p>				

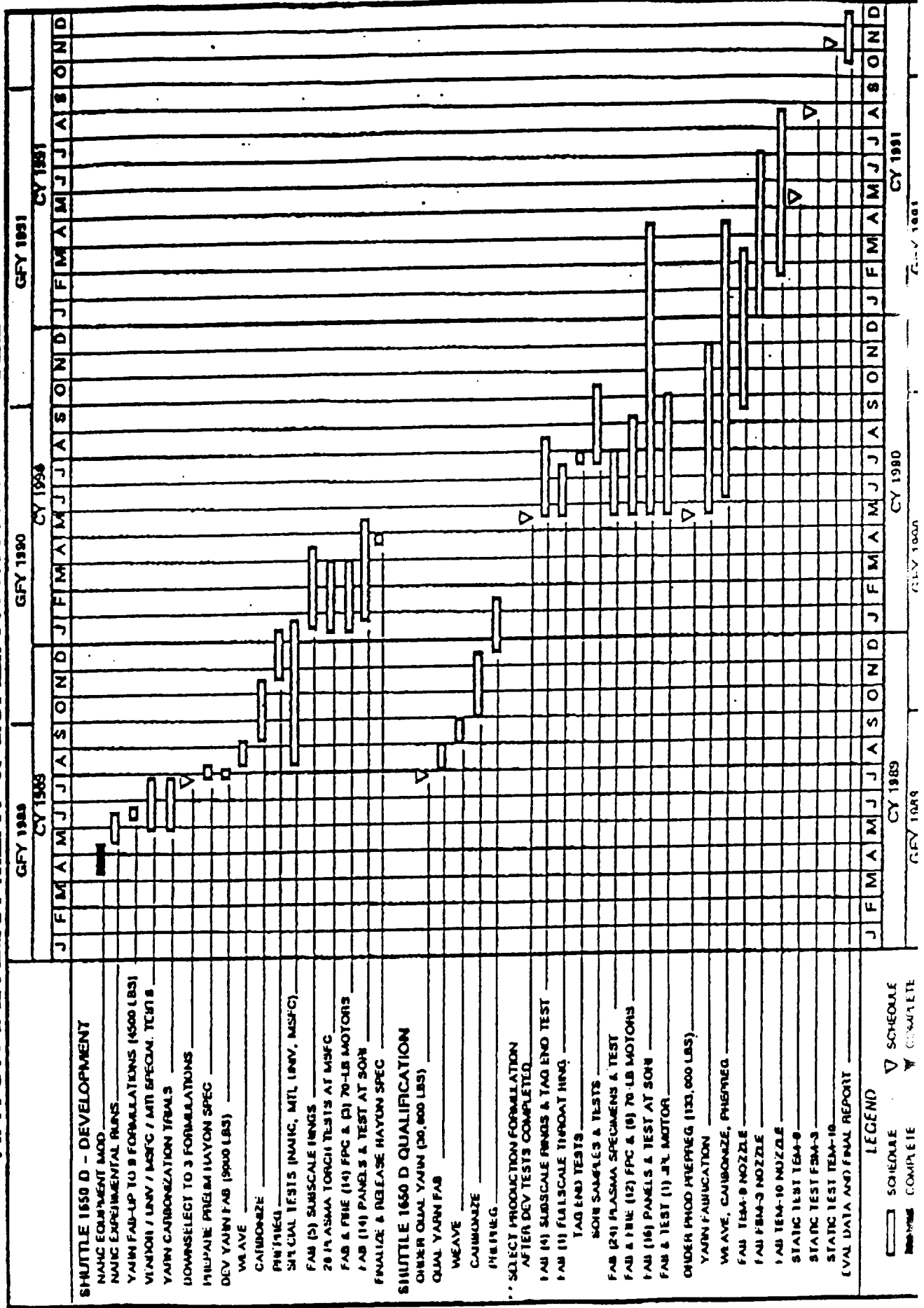
ORGANIZATION: EH34/MSFC	MARSHALL SPACE FLIGHT CENTER NASA 2ND SOURCE RAYON EFFORT	NAME: LOU ANN FIKES
CHART NO.: 11	DATE: MAY 16, 1989	
<p> <u>ADDITIONAL RAYON CHARACTERIZATION TESTS</u> (MTI/W AND MSFC) </p> <ol style="list-style-type: none"> 1. CONDITIONED TENACITY 2. WET TENACITY 3. WET BREAK STRENGTH 4. WT ELONGATION 5. CONDITIONED MODULUS 6. WET MODULUS 7. HEMICELLULOS CONTENT 8. SKIN/CORE RATIO 9. COPPER NUMBER 10. TRACE METAL ANALYSIS 11. SULFATE SULFUR CONTENT 12. S_{6.5} SOLUBILITY 		

..

ORGANIZATION: EH34/MSFC	MARSHALL SPACE FLIGHT CENTER	NAME: LOU ANN FIKES
CHART NO.: 12	NASA 2ND SOURCE RAYON EFFORT	DATE: MAY 16, 1989

RAYON DEVELOPMENT & QUALIFICATION SCHEDULE

REV 18 APR 88



LEGEND
 [] SCHEDULE
 [] COMPLETE
 [] SCHEDULE
 [] COMPLETE

APPENDIX G

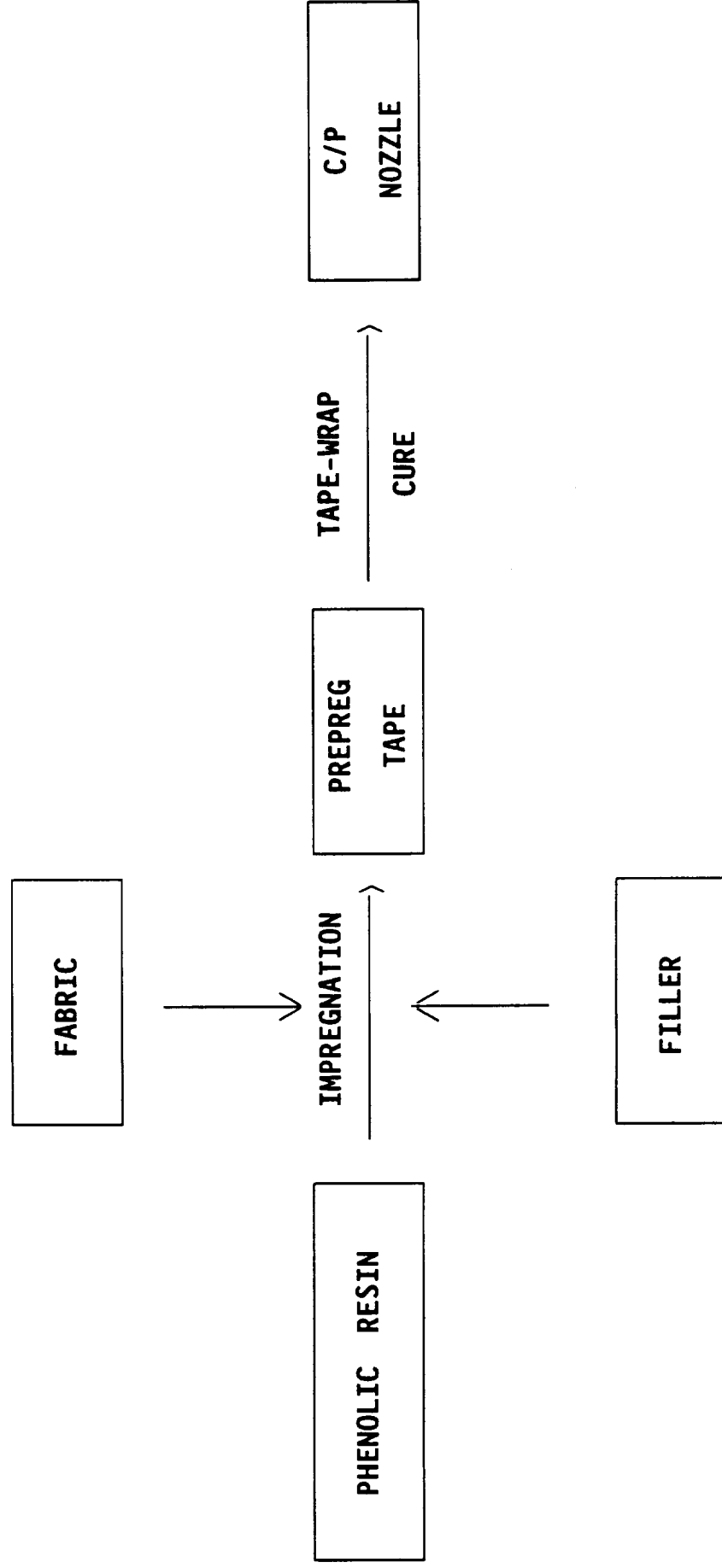
TOM BHE'S PRESENTATION

PHENOLIC RESIN QUALITY CONTROL
BY GEL PERMEATION CHROMATOGRAPHY (GPC)

FOR
ADVISORY COMMITTEE MEETING ON STANDARDIZATION
OF CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS
MAY 16, 1989
SANTA ANA, CA.

S. TOM BHE
PROPULSION ENGINEERING
AEROJET TECHSYSTEMS COMPANY

FIG. 1 / CARBON-PHENOLIC COMPOSITES PROCESSING DIAGRAM

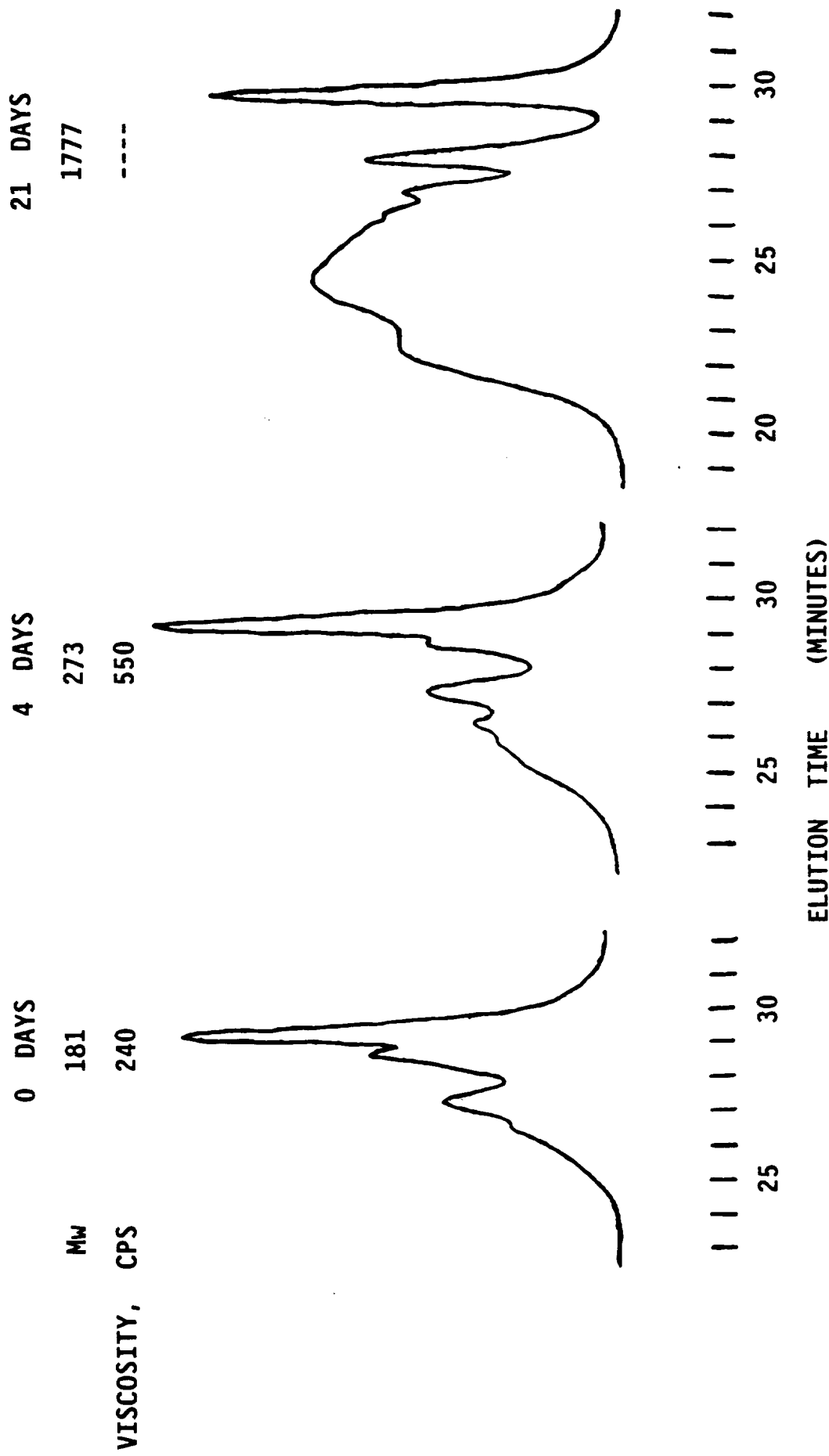


DEGREE OF RESIN ADVANCEMENT AFFECTS PROCESSING & NOZZLE QUALITY

- **PROCESSING**
 - **TAPE-WRAP**
 - **CURE**
- **NOZZLE**
 - **WRINKLE**
 - **DELAMINATION**
 - **COMPACTION**

GPC MEASURES RESIN MOLECULAR WEIGHT (DEGREE OF ADVANCEMENT)

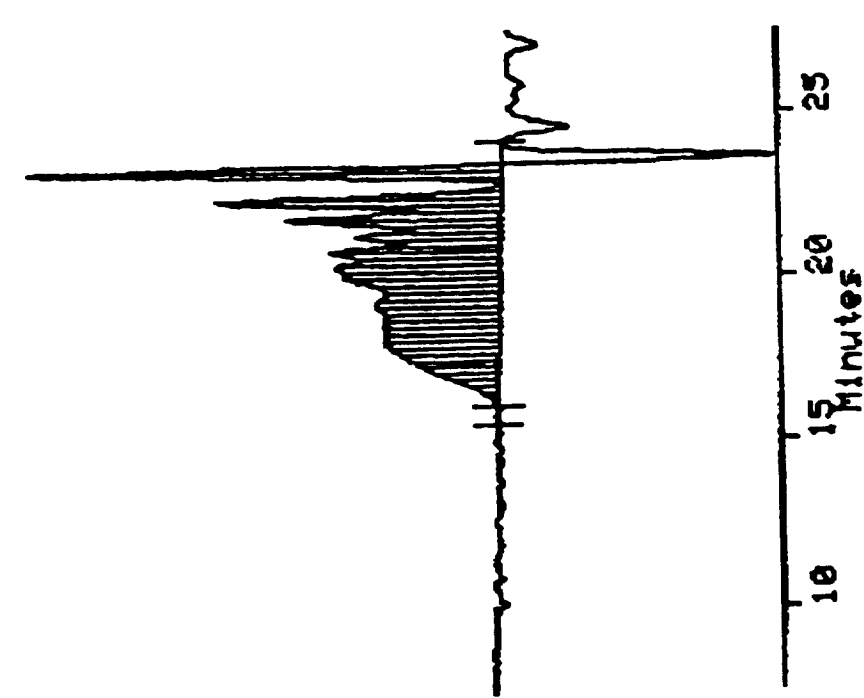
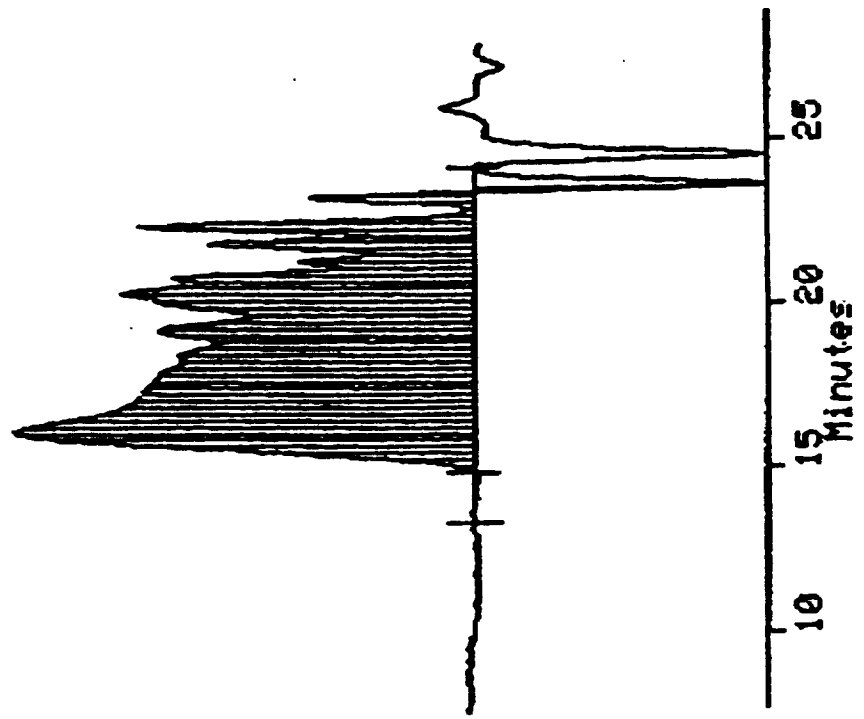
SC 1008 AGING @ 110°F



3 RESIN MOLECULAR WEIGHT INCREASES DURING PREPREGGING

AFTER
M_w = 678

BEFORE
M_w = 411



ELUTION TIME

746 LOT-TO-LOT VARIABILITY OF RESIN M_w

RESIN I			RESIN II		
LOT	RUN NO.	MW	LOT	RUN NO.	MW
A	1	361	A	1	193
	2	389			
	3	405			
	AVG.	385			
B	1	366	B	1	191
	2	372			
	3	370			
	AVG.	369			

CONCLUSIONS

- DEGREE OF STAGING / MOLECULAR WEIGHT OF RESIN AT RESIN MANUFACTURER, PREPREGGER AND NOZZLE FABRICATOR IS CRITICAL IN ENSURING NOZZLE QUALITY.
- GPC IS A GOOD TECHNIQUE FOR DETERMINING RESIN MOLECULAR WEIGHT.
- CURRENTLY, GPC INSTRUMENTATION IS AVAILABLE AT THE RESIN MANUFACTURERS, PREPREGGERS AND NOZZLE FABRICATORS.
- THE PROCEDURE FOR RESIN MOLECULAR WEIGHT MEASUREMENT IS DIFFERENT FROM LABORATORY TO LABORATORY.

RECOMMENDATIONS

- GPC PROCEDURE NEEDS TO BE STANDARDIZED.
- INITIATE ROUND ROBIN TESTING ON M_w DETERMINATIONS BY GPC.
- GENERATE A SUFFICIENT DATA BASE TO DETERMINE THE M_w RANGES REQUIRED AT THE RESIN MANUFACTURERS, PREPREGGERS AND NOZZLE FABRICATORS, TO ENSURE NOZZLE QUALITY.
- INCORPORATE GPC IN THE RESIN & PREPREG ACCEPTANCE SPECIFICATIONS.

APPENDIX H

TOM PARAL'S PRESENTATION

Paul



POLYCARBON, Inc.®

A MEMBER OF THE SIGRI GROUP

May 15, 1989

CARBON ANALYSIS - Leco Corporation

Leco, St. Joseph, Michigan, is the manufacturer of our CR-12 carbon analyzer. They calibrate the CR-12 with a pure compound, sucrose (99.95 + .05% carbon). This is a "working" standard, not a primary standard. However, it is traceable to a NBS (National Bureau of Standards) primary standard.

After they calibrate the CR-12 with sucrose they analyze their secondary standard, petroleum coke. They do this by taking a representative sample from a well-mixed 1000 gram batch. The petroleum coke is analyzed 50 times, then an average is determined. This average, plus two-sigma (two standard deviations) are recorded on aliquot sample bottles then sold for purposes of calibrating customer's CR-12 machine. The total accuracy of the CR-12 carbon analyzer is $\pm 0.5\%$. This includes the accuracy of the petroleum coke calibration sample.

CARBON ANALYSIS - National Bureau of Standards (NBS)

The National Bureau of Standards has had a name change. They are now called the "National Institute of Standards and Technology".

In order to provide laboratories and organizations with carbon reference standards, the NBS will obtain a certain quantity of bituminous coal. They will grind it and thoroughly blend it. Next, they will send aliquots to several different laboratories, who will then analyze the coal by different techniques. Four different techniques are generally used, but no one lab uses all four techniques. The techniques are:

- 1) Infrared Analysis (Leco CR-12 Carbon Analyzer)
- 2) Thermal Conductivity (High Temperature Combustion Technique)
- 3) "Wet" Chemical Analysis (Coulometric Analysis)
- 4) Gravimetric Analysis (Combustion-train Technique)

After obtaining the carbon analysis from the different laboratories, using the four different analytical techniques, they will average the values. They will then use the average carbon value as the stated carbon value for that batch of coal (or SRM). Finally, they will sell samples of this material to laboratories as a "NBS Traceable Reference Standard".

APPENDIX I

ERIC STOKES' PRESENTATION

**A PROCEDURE FOR THE
MEASUREMENT OF FIBER, FILLER AND RESIN CONTENT
IN FULLY CURED CARBON/PHENOLIC COMPOSITES**

**PRESENTED TO THE ADVISORY COMMITTEE ON STANDARDIZATION
OF CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS**

SANTA ANA, CALIFORNIA

MAY 16, 1989

ERIC STOKES



ACKNOWLEDGEMENTS

HOLLIS HILL - SOUTHERN RESEARCH INSTITUTE

JOHN R. KOENIG - SOUTHERN RESEARCH INSTITUTE

DR. RAYMOND CLINTON - NASA/MSFC

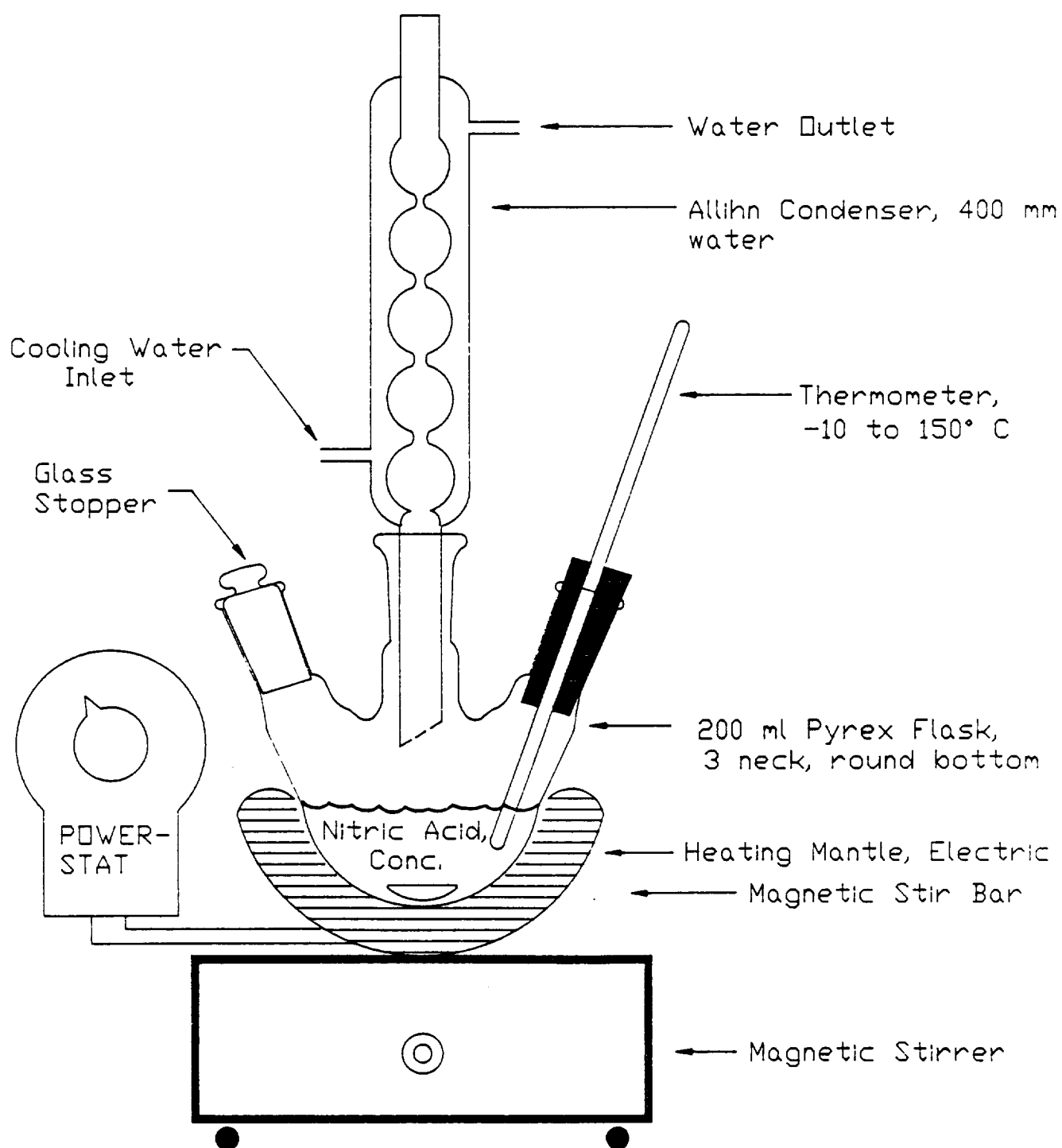
REFERENCES

1. SULFURIC ACID/HYDROGEN PEROXIDE
 - HAYNES, W.H. AND T.L. TOLBERT
"DETERMINATION OF THE GRAPHITE FIBER CONTENT OF PLASTIC COMPOSITES," J. COMPOSITE MATERIALS 3:709-712, 1969.
2. OXIDATION AT 390-420 OC
 - "CARBON FIBRES, THEIR COMPOSITES AND APPLICATIONS" PLASTIC INSTITUTE, LONDON, 1971, P. 188.
3. NITRIC ACID DIGESTION
 - R. J. KUH BANDER, "DETERMINING FIBER CONTENT OF GRAPHITE YARN-PLASTIC COMPOSITES," AFML-TR-67-243, 1967.
4. MOISTURE RELEASED ON COMBUSTION
 - H. SWIFT, "DETERMINATION OF THE RESIN CONTENT OF CARBON FIBRE-RESIN COMPOSITES" ANALYST 103:990-993, 1978.
5. POTASSIUM HYDROXIDE/ETHYLENE GLYCOL SOLUTION
 - FIBERITE CORP., QUALITY CONTROL METHOD R-21.

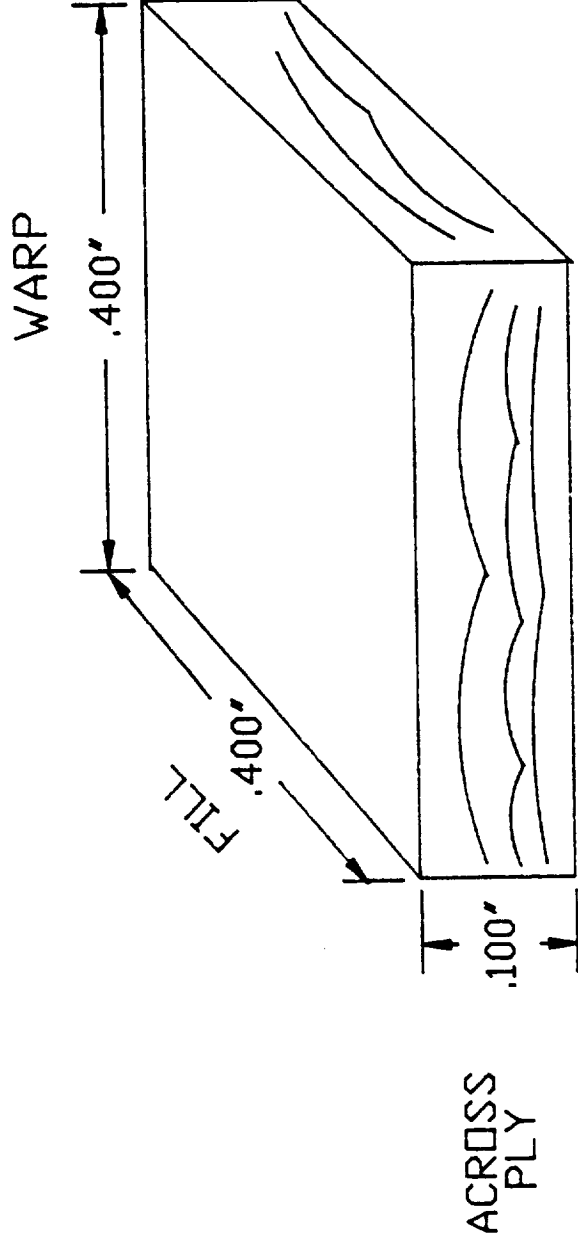
PROPOSED METHODS FOR DETERMINING RESIN CONTENT IN FULLY CURED CARBON/PHENOLIC COMPOSITES

- 1. SULFURIC ACID/HYDROGEN PEROXIDE DIGESTION**
 - DANGER OF EXPLOSION
 - CARBON FIBER MAY BE AFFECTED
 - ADDITION OF HYDROGEN PEROXIDE IS DONE DROPWISE TAKING SEVERAL HOURS (VERY SLOW AND TEDIOUS)
- 2. OXIDATION AT 390-420 OC**
 - LARGE DECREASE IN MASS OF THE GRAPHITE FIBERS AT THESE TEMPERATURES
 - K FACTOR MAY VARY
- 3. NITRIC ACID DIGESTION**
 - DOES NOT WORK ON ALL RESIN SYSTEMS
- 4. MOISTURE RELEASED ON COMBUSTION**
 - REQUIRES PURE RESIN OF SAME COMPOSITION AND DEGREE OF CURE
- 5. POTASSIUM HYDROXIDE/ETHYLENE GLYCOL SOLUTION**
 - UNTESTED

SCHEMATIC OF EXPERIMENTAL APPARATUS FOR NITRIC ACID DIGESTION OF CARBON PHENOLIC COMPOSITES



SCHEMATIC OF SPECIMEN USED IN THE ACID DIGESTION
PROCEDURE FOR THE DETERMINATION OF
RESIN CONTENT IN CARBON PHENOLIC COMPOSITES



FIBER CONTENT

- 1. 100 ML OF CONCENTRATED NITRIC ACID TO FLASK**
- 2. HEAT TO DESIRED TEMPERATURE WITH STIRRING**
- 3. WHEN TEMPERATURE EQUILIBRATES ADD PRE-WEIGHED SPECIMEN AND CONTINUE STIRRING**
- 4. AFTER ALLOTTED TIME HAS PAST, QUENCH FLASK IN ICE BATH**
- 5. FILTER ACID AND SPECIMEN THROUGH A PREDRIED AND TARED 47MM DIAMETER 1.0 μ M PORE SIZE GLASS FIBER FILTER UNDER SUCTION (GELMAN #S61631)**
- 6. TRANSFER FILTER FUNNEL TO NEW FILTER FLASK**
- 7. RINSE WITH 400 ML H₂O**
- 8. RINSE WITH 20 ML ACETONE**
- 9. PLACE FILTER IN PRETARED AL. BOAT AND DRY AT 120 °C OVERNIGHT**

FIBER CONTENT (CONTINUED)

- 10. COOL TO ROOM TEMPERATURE IN DESICCATOR**
- 11. RECORD WEIGHT OF PAN, FILTER PAPER, AND SAMPLE**
- 12. SUBTRACT WEIGHT OF FILTER PAPER AND PAN TO GET WEIGHT OF FIBERS.**

FILLER CONTENT (CONTINUED)

- 8. DRY AT 120 OC OVERNIGHT (FOUR HOURS)**
- 9. COOL IN DESICCATOR**
- 10. WEIGH FILTER PAPER**
- 11. SUBTRACT FILTER PAPER WEIGHT FROM SAMPLE AND FILTER PAPER TO GET WEIGHT OF FILLER**

FLOW CHART OF NITRIC ACID DIGESTION PROCEDURE

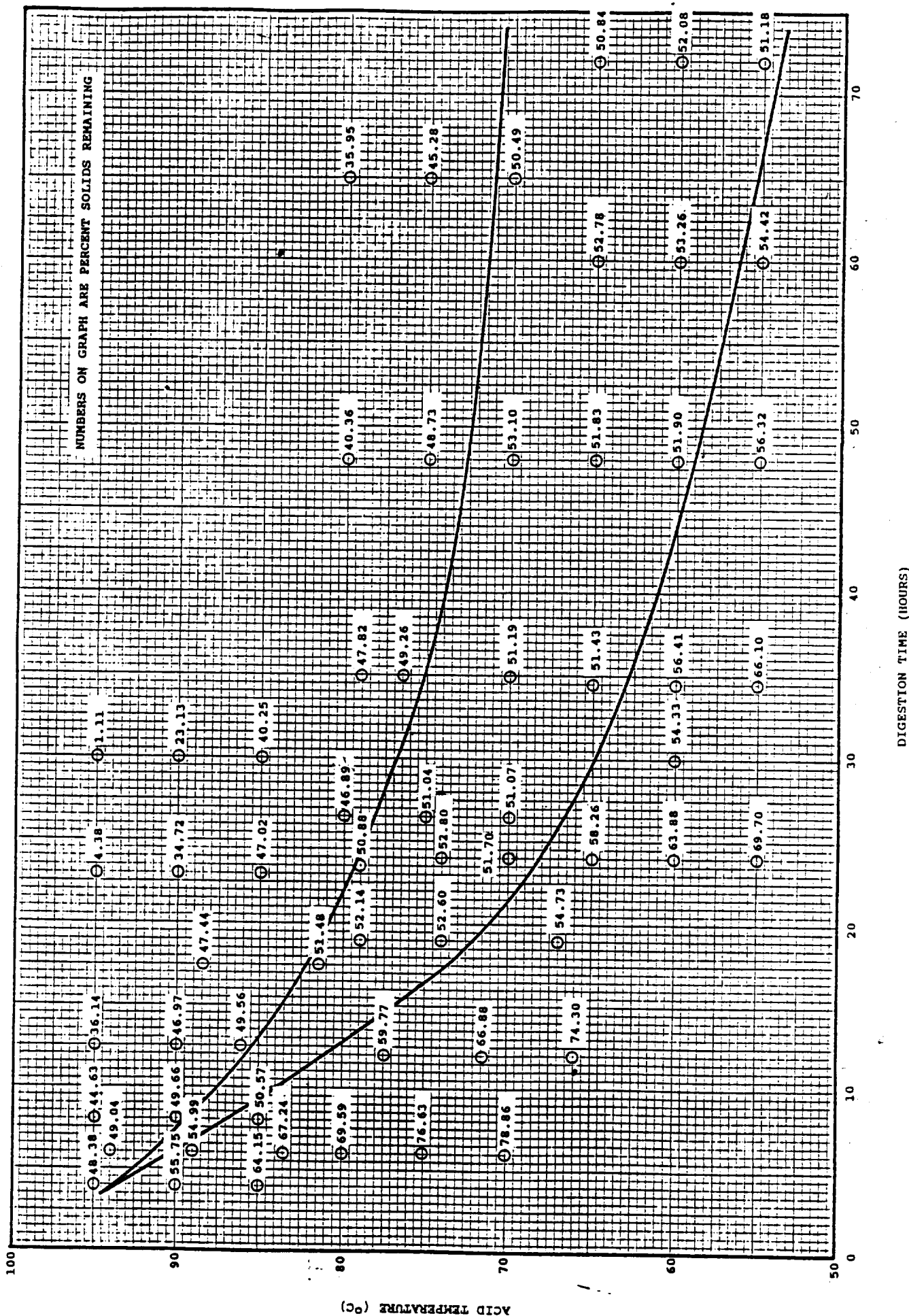
```

graph TD
    Specimen[Specimen  
.4 x .4 x .1"] --> WeighSpec[WEIGH]
    WeighSpec --> FilterPaper1[Filter Paper]
    FilterPaper1 --> Dry1[Dry]
    Dry1 --> Cool1[Cool]
    Cool1 --> Weigh1[Weigh]
    Weigh1 --> Composite[Composite Sample Weight]
    
    100M[100 M  
CONC. HNO3] --> Heat[HEAT TO  
TEMP]
    Heat --> Digest[DIGEST]
    Digest --> Quench[QUENCH]
    Quench --> Filter[Filter]
    Filter --> Aluminum[ALUMINUM  
MOUNT]
    Aluminum --> Dry2[Dry]
    Dry2 --> Cool2[Cool]
    Cool2 --> Weigh2[Weigh]
    Weigh2 --> Fiber[Fiber Weight]
    
    Filter --> Transfer[TRANSFER FILTER  
TO NEV FLASK]
    Transfer --> Water[Water  
RINSE]
    Water --> Acetone[Acetone  
RINSE]
    Acetone --> Dry3[Dry]
    Dry3 --> Cool3[Cool]
    Cool3 --> Weigh3[Weigh]
    Weigh3 --> Resin[Resin Weight]
    
    Filter --> Settle[SETTLE]
    Settle --> Recant1[RECAN'T  
90-100 M]
    Recant1 --> Discard1[DISCARD]
    Discard1 --> Acetone1[Acetone]
    Acetone1 --> AddDrop[ADD DROP WISE  
TO FILTER PAPER]
    AddDrop --> Dry4[Dry]
    Dry4 --> Cool4[Cool]
    Cool4 --> Weigh4[Weigh]
    Weigh4 --> Filler[Filler Weight]
    
    Settle --> Centrifuge[CENTRIFUGE]
    Centrifuge --> Recant2[RECAN'T]
    Recant2 --> Discard2[DISCARD]
    Discard2 --> Acetone2[Acetone]
    Acetone2 --> AddDrop
    
    Settle --> FilterPaper2[Filter Paper]
    FilterPaper2 --> Dry5[Dry]
    Dry5 --> Cool5[Cool]
    Cool5 --> Weigh5[Weigh]
    Weigh5 --> Composite
  
```

The flowchart details the nitric acid digestion procedure. It begins with weighing a specimen (.4 x .4 x .1) and placing it on filter paper to dry, cool, and weigh, contributing to the composite sample weight. The specimen is then digested with 100 M concentrated nitric acid (HNO₃), heated to temperature, and quenched. The resulting material is filtered and can be weighed directly on an aluminum mount to determine fiber weight, or it can be transferred to a Nesslerization Flask (NEV) for further processing. In the NEV flask, it is rinsed with water and acetone, then dried, cooled, and weighed to determine resin weight. Alternatively, the material can be settled, and the supernatant (recant) can be discarded and rinsed with acetone, added dropwise to the filter paper, and then dried, cooled, and weighed to determine filler weight. The settled material can also be centrifuged and the recant discarded and rinsed with acetone, added dropwise to the filter paper, and then dried, cooled, and weighed to determine filler weight. Finally, the material on the filter paper is dried, cooled, and weighed to contribute to the composite sample weight.

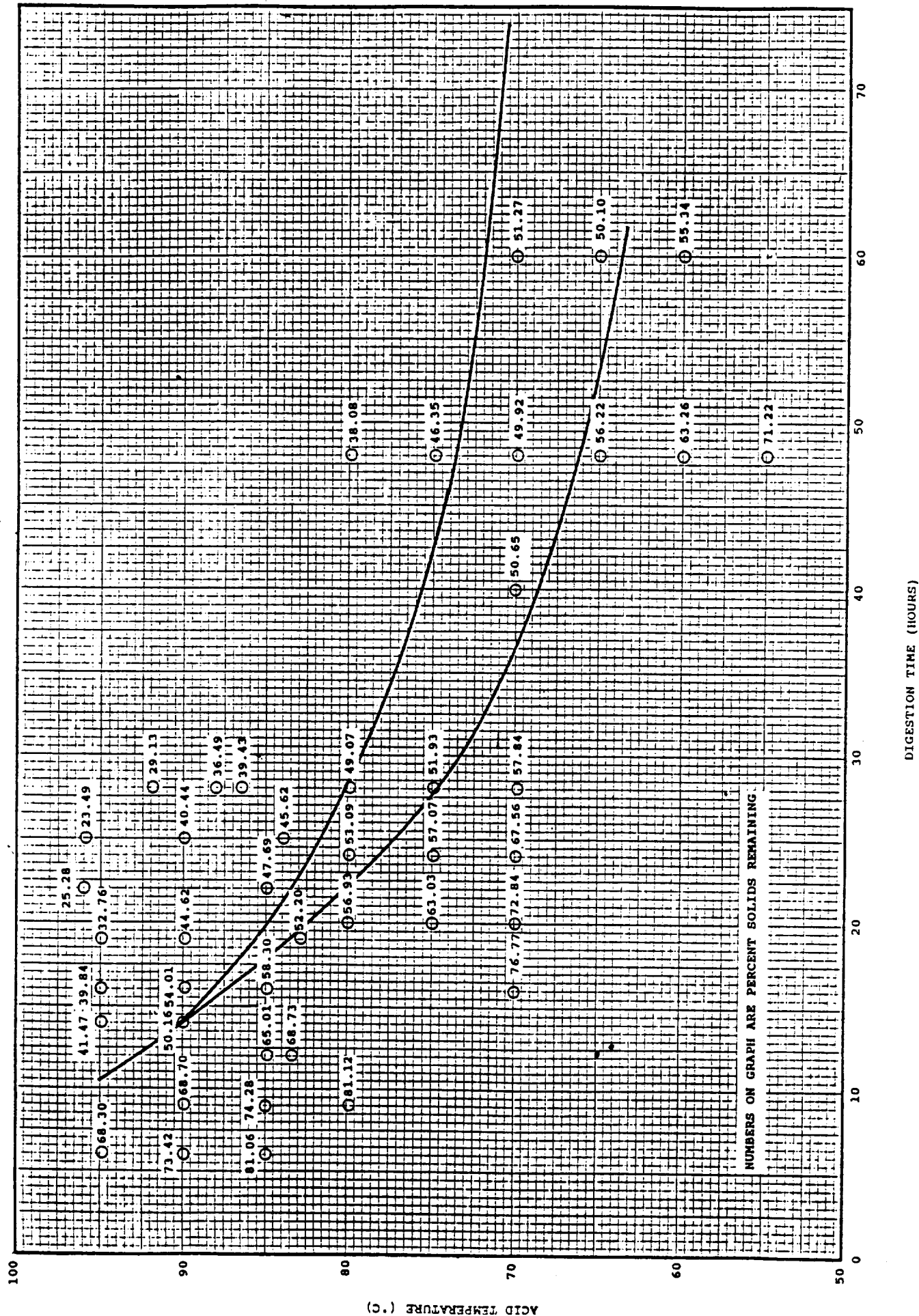
NITRIC ACID DIGESTION OF FM 5055 CARBON-PHENOLIC COMPOSITE.

(MEAN 350°F VOLATILES CONTENT = 4.28%)

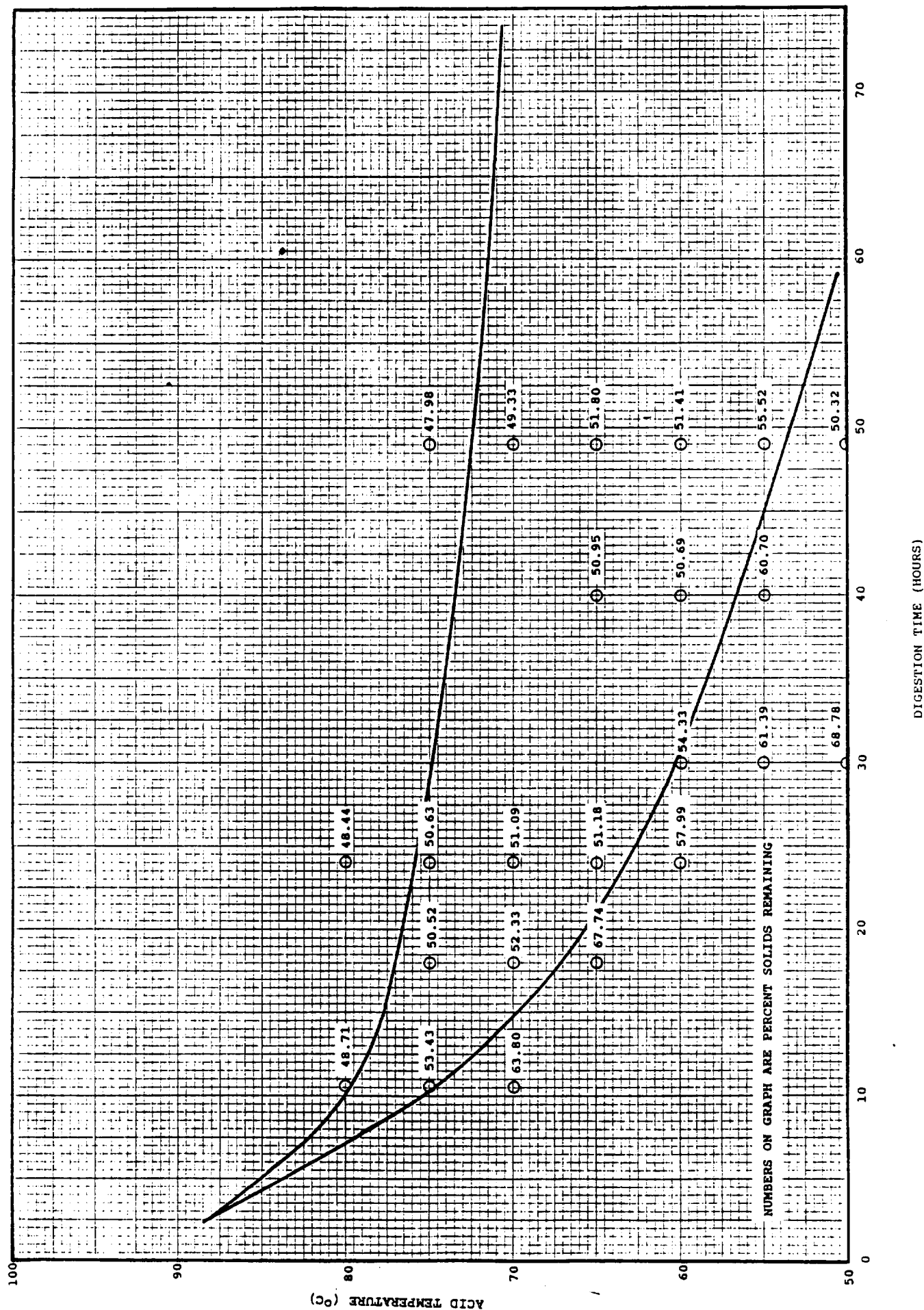


NITRIC ACID DIGESTION OF FM 5055 CARBON-PHENOLIC COMPOSITE.

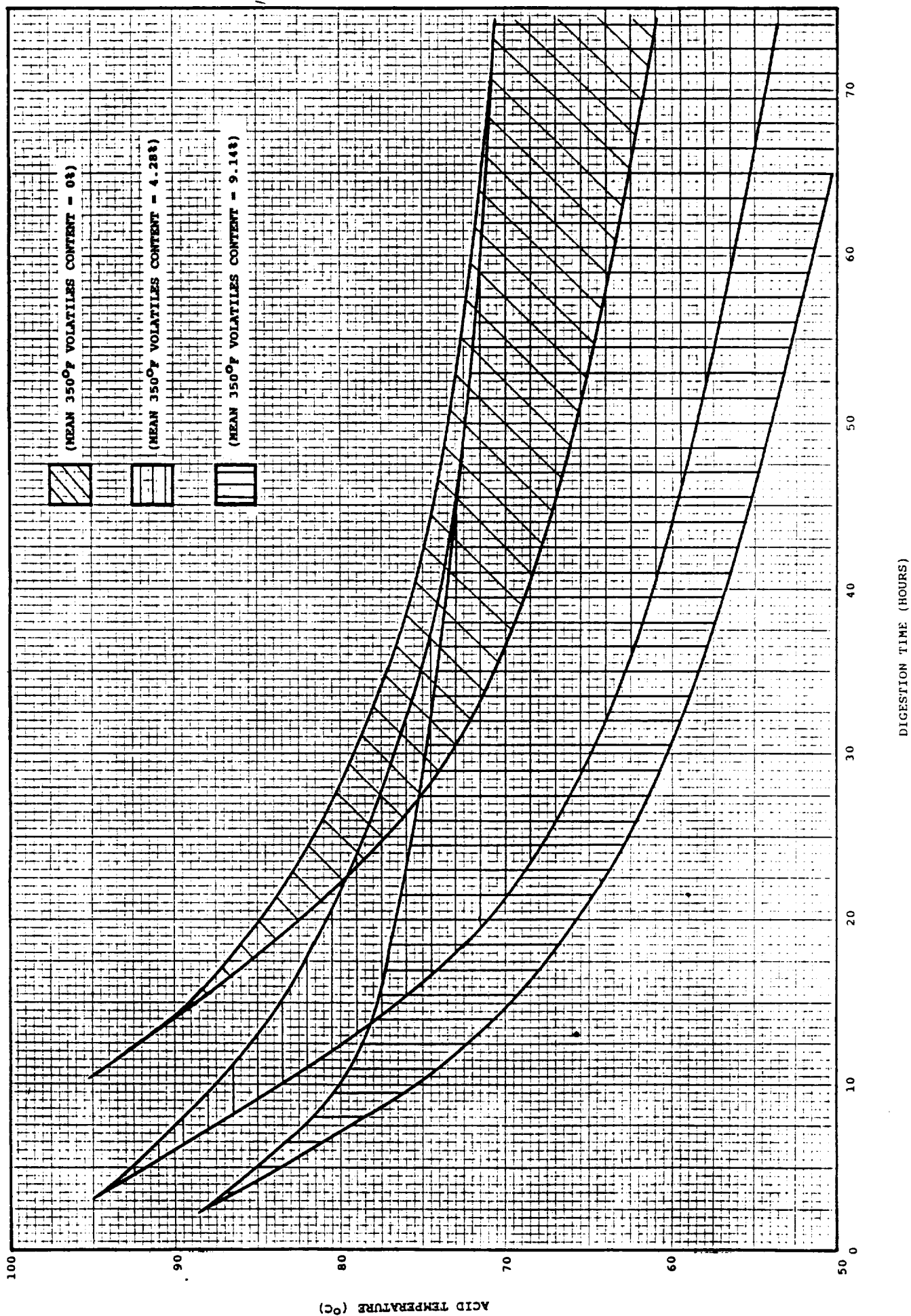
(MEAN 350°F VOLATILES CONTENT = 0%)

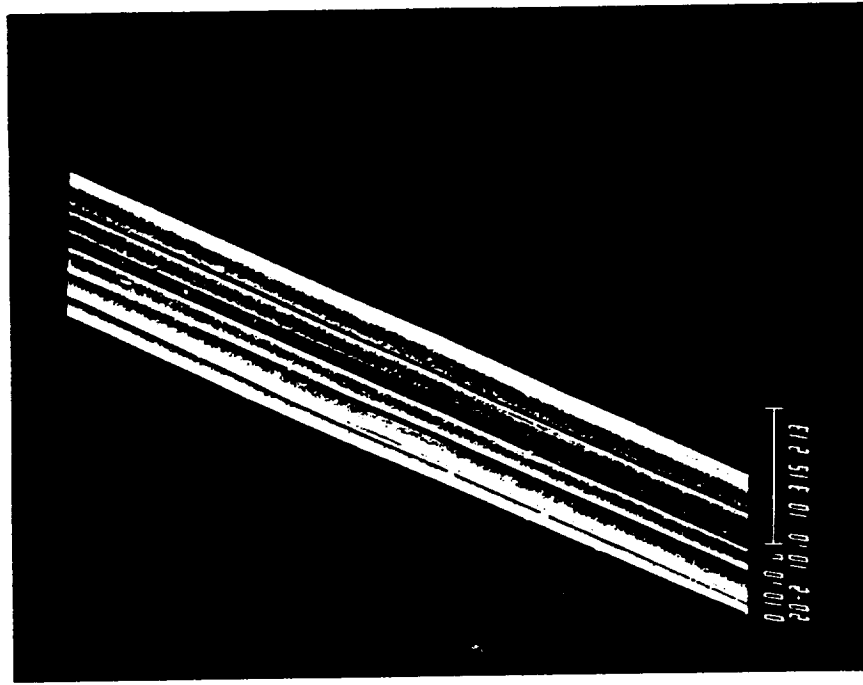


NITRIC ACID DIGESTION OF FM 5055 CARBON-PHENOLIC COMPOSITE.
(MEAN 350°F VOLATILES CONTENT = 9.14%)

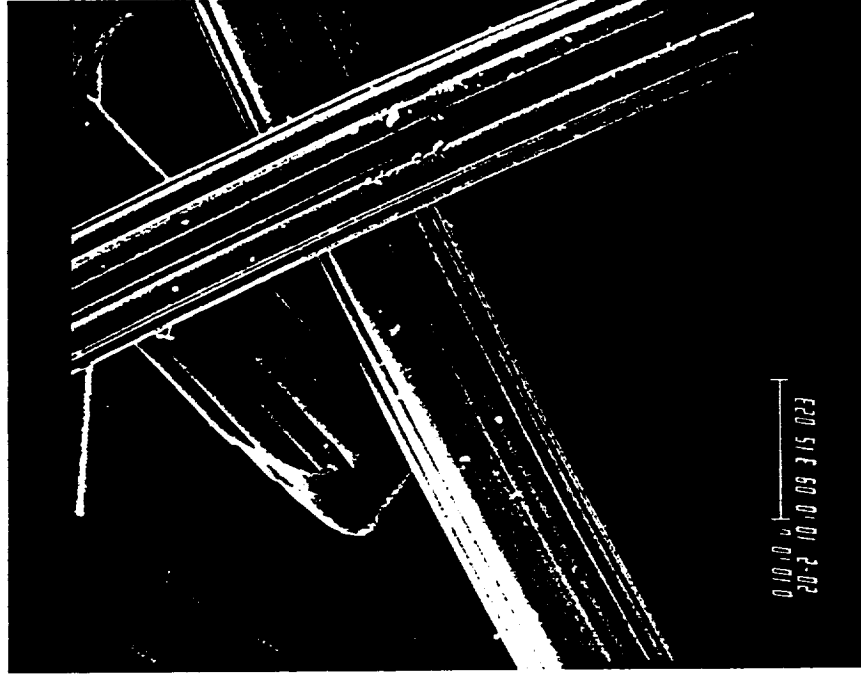


NITRIC ACID DIGESTION OF FM 5055 CARBON-PHENOLIC COMPOSITE.

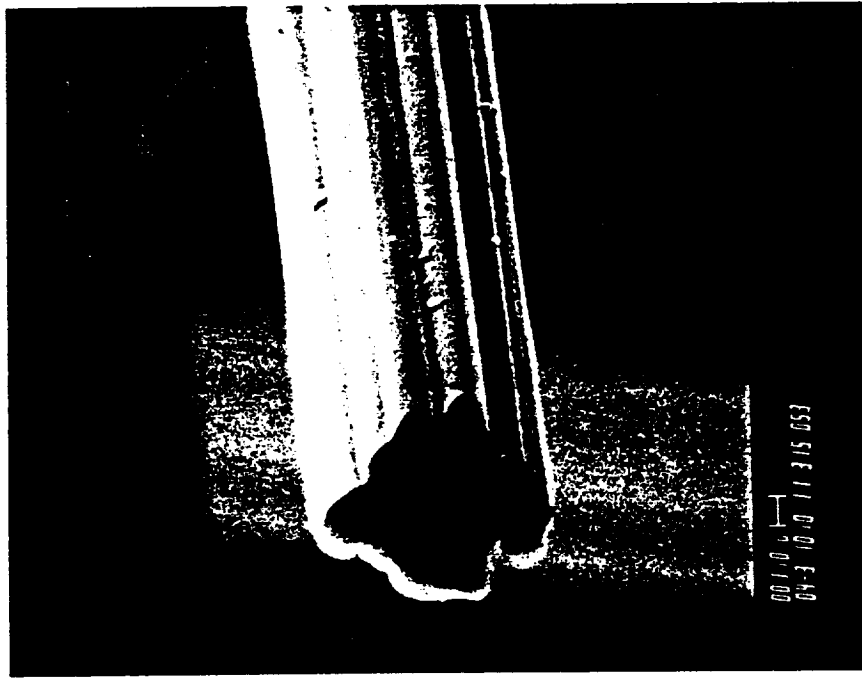




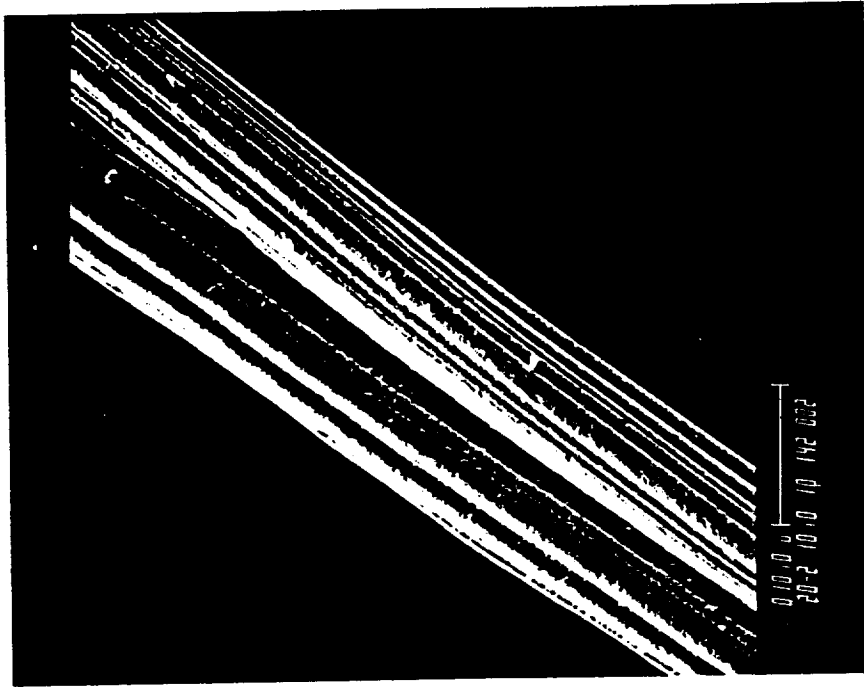
VIRGIN CCA-3 FIBER



**48 HOURS/65 OC (WET)
100 % OF FIBER WEIGHT RECOVERED**



72 HOURS/65 OC
(AS RECEIVED)
100% OF FIBER WEIGHT
RECOVERED



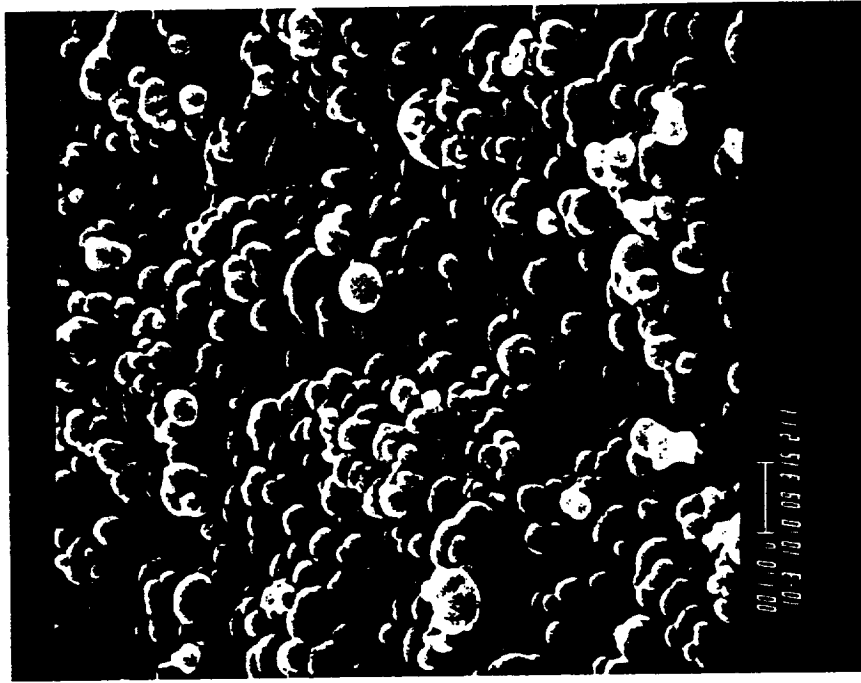
23 HOURS/90 OC
(AS RECEIVED)
69% OF FIBER WEIGHT
RECOVERED



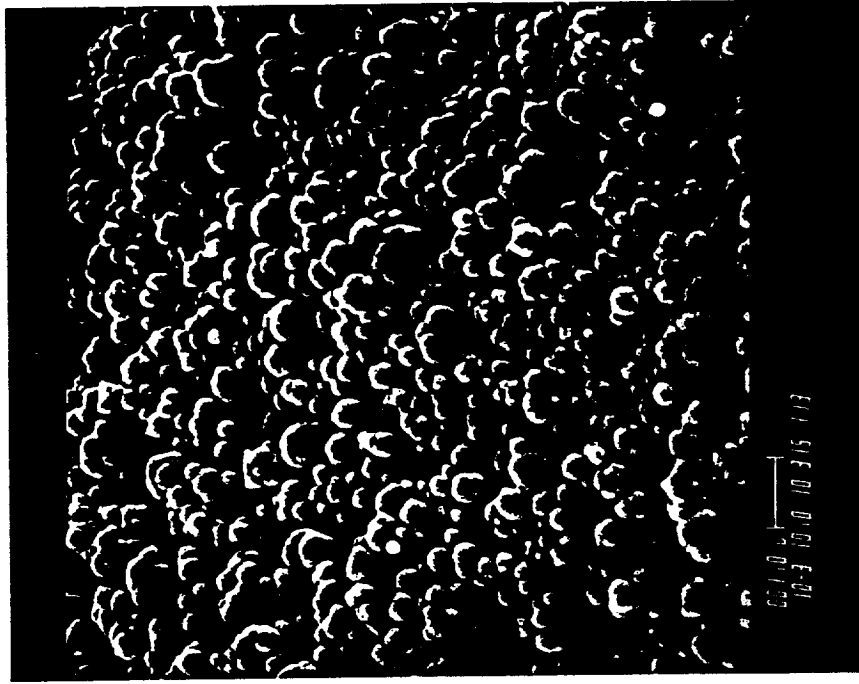
30 HOURS/90 OC
(AS RECEIVED)
45% OF FIBER WEIGHT
RECOVERED



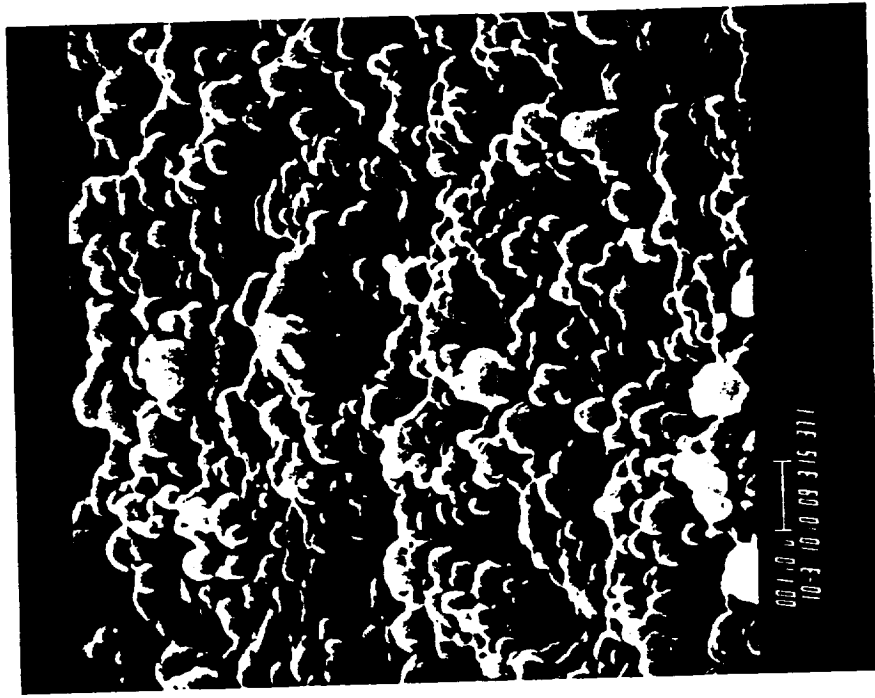
13 HOURS/95 OC
(AS RECEIVED)
12.5% OF FIBER WEIGHT
RECOVERED



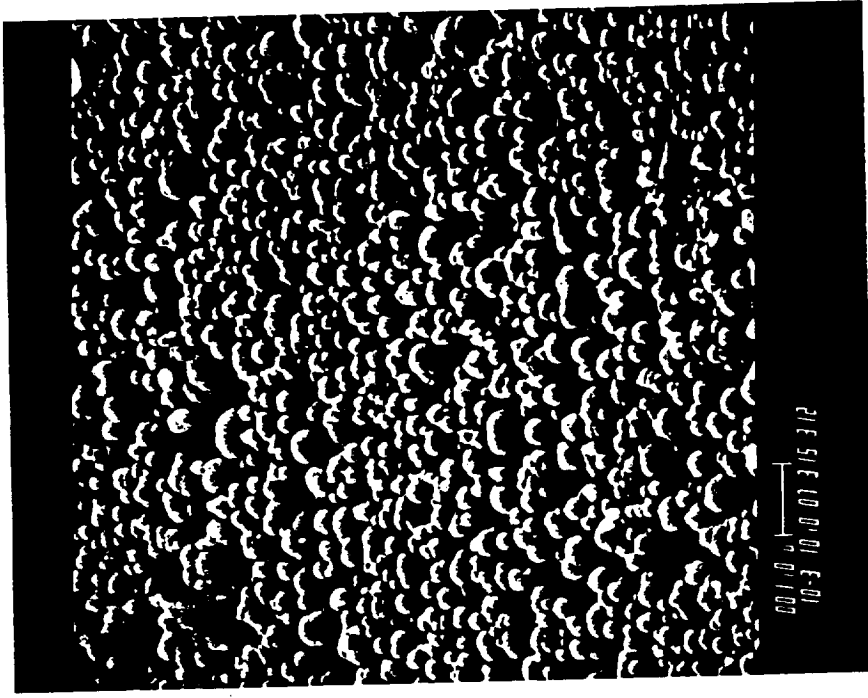
VIRGIN FIBERITE 7068
CARBON FILLER



24 HOURS/70 OC (WET)
100% OF FIBER WEIGHT
RECOVERED



**13 HOURS/95 °C
(AS RECEIVED)
12.5% OF FIBER WEIGHT
RECOVERED**



**48 HOURS/80 °C (DRY)
75% OF FIBER WEIGHT
RECOVERED**

RECOVERY OF FILLER FROM FM5055 CARBON - PHENOLIC COMPOSITE
WITH THE NITRIC ACID DIGESTION PROCEDURE

SAMPLE I.D.	STARTING CONDITION	DIGESTION		CENTRIFUGATION OR SEDIMENTATION	AS REC	
		TIME (hours)	TEMP (deg C)		FILLER %	FIBER %
35-3	DRY	40	70	C	13.99	50.65
34-2	DRY	66	65	C	14.90	50.10
34-3	DRY	66	70	S	15.21	51.27
31-3	DRY	48	80	C	14.63	49.92
25-2	WET	48	70	S	15.56	51.80
25-3	WET	48	75	C	14.64	49.33
20-3	WET	40	60	C	13.81	50.95
18-3	WET	24	70	S	14.32	51.09
<hr/>						
MAX. VALUE					15.56	51.80
MIN. VALUE					13.81	49.33
MEAN					14.63	50.64
ST. DEV.					0.55	0.76
COEFF. OF VAR.					3.78%	1.49%

CONTROLLED EXPERIMENTS
(CCA-3 FIBER AND 7068 FILLER)

EXPERIMENT	TEMPERATURE (deg C)	DIGESTION TIME (hours)	CENTRIFUGATION OR SEDIMENTATION	RECOVERY		TOTAL RECOVERY (%)
				AS FIBERS (%)	AS FILLER (%)	
(24-1)	70	24	C	100.96	92.90	98.31
(36-1)	70	30	C	101.05	92.19	98.90
(36-2)	70	30	C	99.21	93.37	97.86

95 OC/13 HOUR DIGESTION (AS RECEIVED)

PERCENT OF SAMPLE

SAMPLE ID	FILLER RECOVERY	FIBER RECOVERY	TOTAL RECOVERY	EFFICIENCY %
37-1	27.34	6.44	33.77	51

CONCLUSIONS

- **NITRIC ACID DIGESTION CAN BE USED TO QUANTIFY THE ABSOLUTE AMOUNTS OF FIBER, FILLER, AND RESIN IN CARBON/PHENOLIC COMPOSITES**
- **DIGESTION AT TEMPERATURES AT OR BELOW 70 OC ARE REQUIRED TO QUANTITATIVELY RECOVER CARBON FIBER**
- **DIGESTION AT TEMPERATURES ABOVE 80 OC RESULTS IN VISABLE EVIDENCE OF FIBER PITTING**
- **DIGESTION AT TEMPERATURES ABOVE 80 OC RESULTS IN SOME CHEMICAL DISSOLUTION OF CARBON FIBERS**
- **DIGESTION OF CARBON-PHENOLIC BY NITRIC ACID IS SENSITIVE TO THE MOISTURE CONTENT OF THE COMPOSITE**
- **TO ELIMINATE THE AFFECT OF MOISTURE ON THE ACCURACY OF THE PROCEDURE A STANDARD DIGESTION TIME OF 48 HOURS AND TEMPERATURE OF 70 OC IS RECOMMENDED WITH 0.4" (WARP) X 0.4" (FILL) X 0.1 (A/P) SPECIMENS**

CONCLUSIONS (CONTINUED)

- **THE PROCEDURE REQUIRES ONLY A SMALL AMOUNT OF MATERIAL**
- **THE PERFORMANCE OF THIS PROCEDURE IS NOT LABOR INTENSIVE, AND CAN BE PERFORMED BY PERSONNEL WITH A LIMITED AMOUNT OF TRAINING.**
- **THE PROCEDURE IS NEARLY INSENSITIVE TO MODERATE FLUCTUATION IN DIGESTION TIME AND TEMPERATURE**

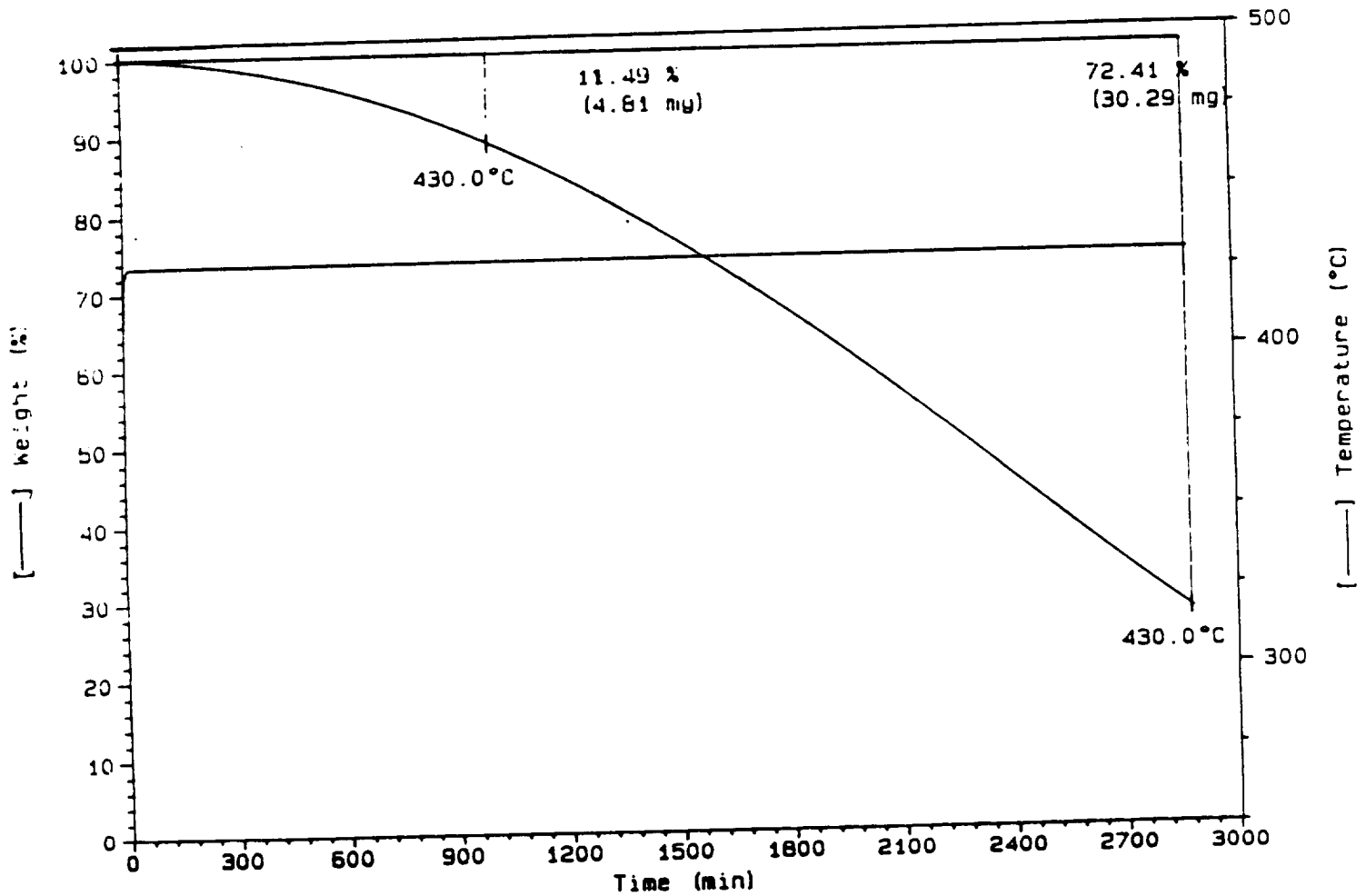
DESCRIPTION OF BLUE M'S ULTRATEMP INERT GAS OVENS

<u>MODEL NUMBER</u>	<u>INSIDE DIMENSIONS</u> <u>(INCHES)</u>			<u>OVERALL DIMENSIONS</u> <u>(INCHES)</u>			<u>VOLUME</u> <u>(FT³)</u>	<u>PRICE</u> <u>(\$)</u>
	<u>WIDTH</u>	<u>DEPTH</u>	<u>HEIGHT</u>	<u>WIDTH</u>	<u>DEPTH</u>	<u>HEIGHT</u>		
IGF-6680F-4	20	18	20	46	35	76	4.1	7,300
IGF-7780F-4	25	20	20	53	37	76	5.8	8,200
IGF-8880F-4	38	20	25	93*	36	72	11.0	10,400
IGF-9980F-4	48	24	36	102*	40	83	24.0	13,800

* INCLUDES 25" FOR A SIDE-MOUNTED CONTROL UNIT.

ACCELERATED OXIDATION TEST CONDITIONS

- Equipment - Blue M Oven IGF-7780-4
- Temperature - 430° C
- Atmosphere - Flowing Oxygen
- Time - 16 Hours
- Number of Samples - 72
- Fiber Weight - 3 Grams



TGA Weight Loss Curve for T-650/42, Trace 12F0821, 48 Hours in Oxygen at 430°C. Typical for T-650/42, T-300R type of carbon yarn.

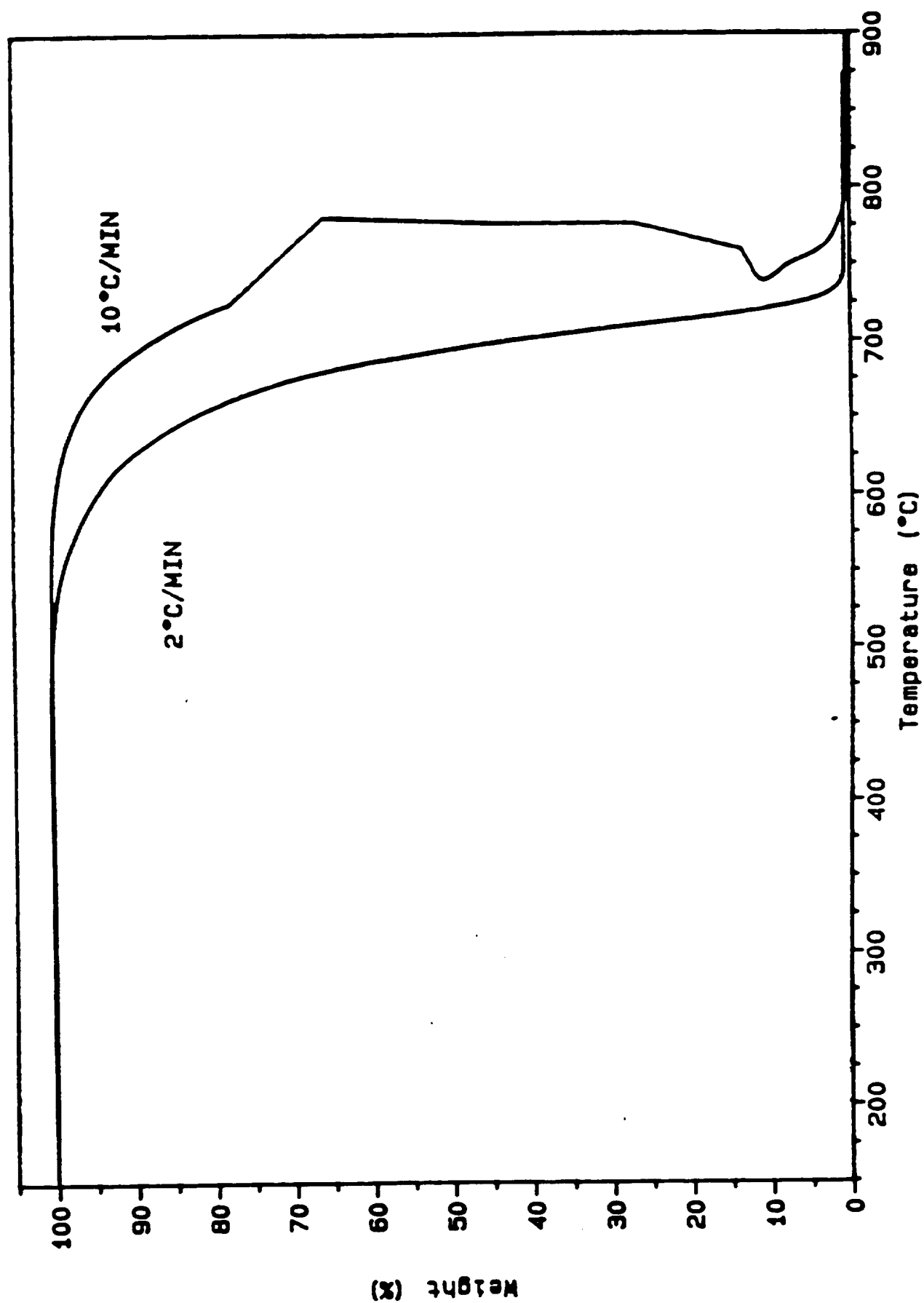
PERCENT OXIDATIVE WEIGHT LOSSES OF CARBON YARNS AND CLOTHS

MATERIAL	NOTEBOOK REF. 163-	TRACE	WEIGHT LOSS IN AIR AT				WEIGHT LOSS IN OXYGEN	
			316°C 1000 HOURS	375°C 1000 HOURS	525°C 1/2 HOUR	525°C 2 HOURS	430°C 1000 MIN.	430°C 48 HOURS
T-300R 12K	39-82-5	12F0607R	4.6	93.6	1.38	5.22	11.7	NYA
T-300R 12K	37-81-6	12E1217R	3.1	88.0	1.11	3.40	12.5	NYA
T-300R 3K	37-81-3	NONE	3.0	82.1	0.77	2.81	14.7	NYA
T-300 3K	39-78-1	3F0407	5.1	98.0	3.47	12.2	16.7	NYA
T-650/42 12K	39-82-9	12F0821	4.6	----	0.46	2.94	13.8, 12.2	NYA
CELION IMA-7	39-82-11	LOT 5Y62	----	13.5	1.67	2.70	2.68, 3.62	8.36
T-40R 3K	39-78-3	Q51215	0.13	2.3	0.44, 0.31	2.97	1.12, 0.50, 0.37	2.72
T-40R 12K	39-78-4 37-81-15	Q51216	0.16	2.7	0.68	2.88	0.99, 0.83	2.64
T-40R 12K	39-82-6	Q60625	0.20	1.64	0.78	3.31	0.63	NYA
VCK CARBON CLOTH	-----	5C4-4, #335	----	----	2.48	35.9	76.1	----
VCL CARBON CLOTH*	-----	LOT 4C4-4, #93	----	----	32.2	**	***	----
VCL CARBON CLOTH*	-----	(1983)	----	----	38.5	----	----	----
WCA GRAPHITE CLOTH	-----	LOT 5C4, #358	----	----	0.08	0.11	0.30	----
WCG GRAPHITE CLOTH	-----	LOT 5C6-1, #476	----	----	0.27	0.50	0.42	----

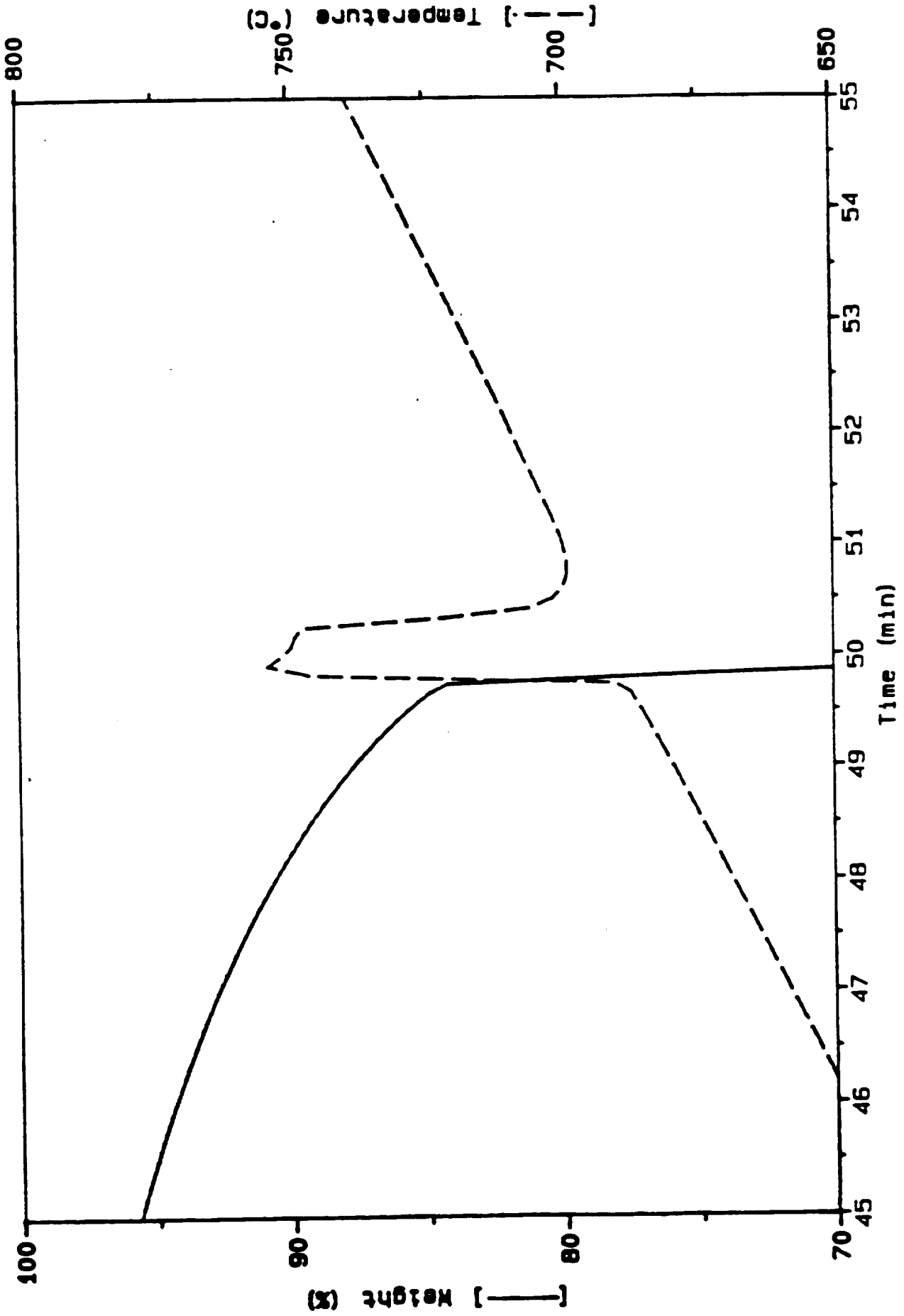
* THIS CLOTH CONTAINS ABOUT 0.1% SODIUM.

** 100% WEIGHT LOSS IN 72 MINUTES.

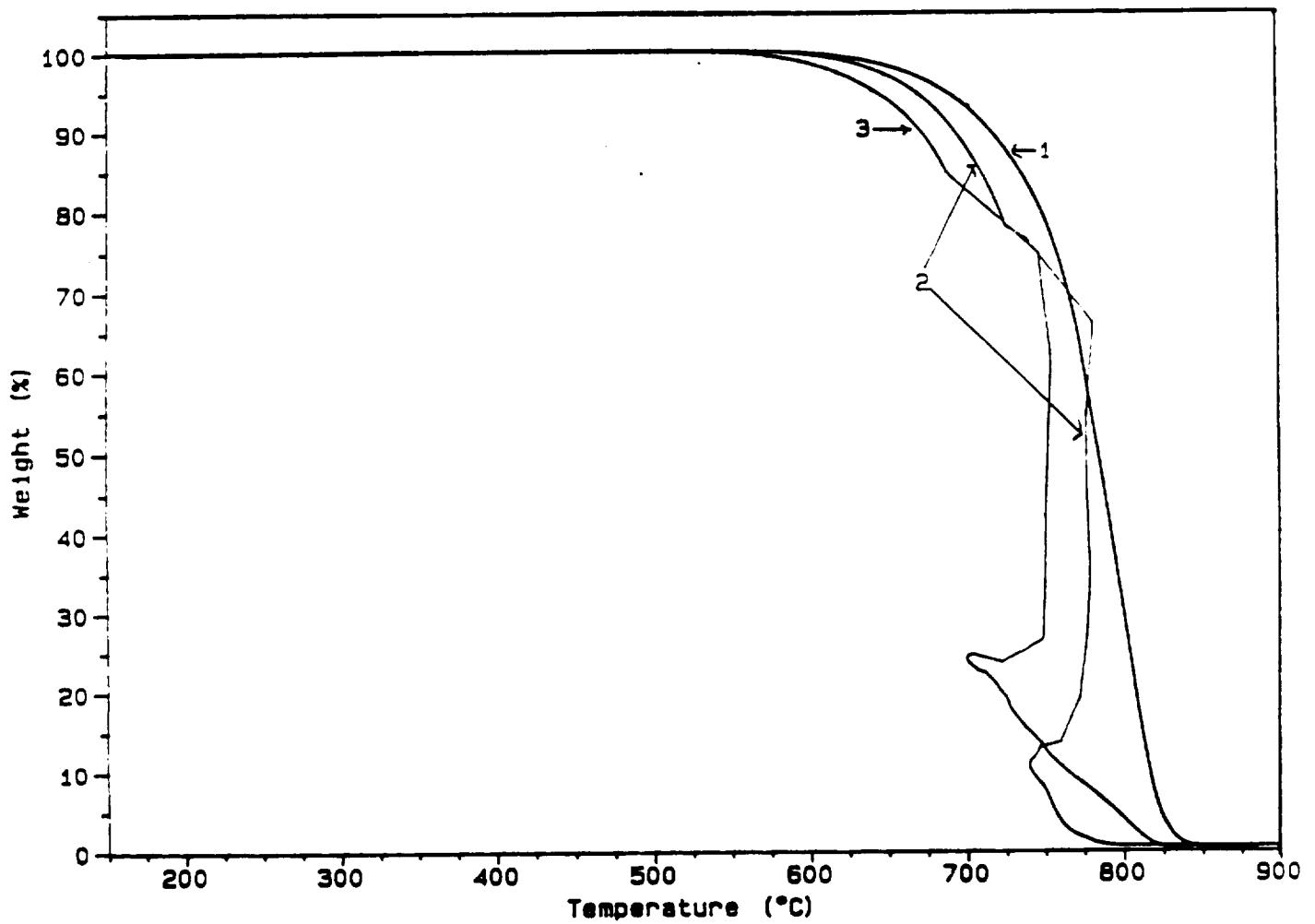
*** 97% WEIGHT LOSS IN 400 MINUTES.



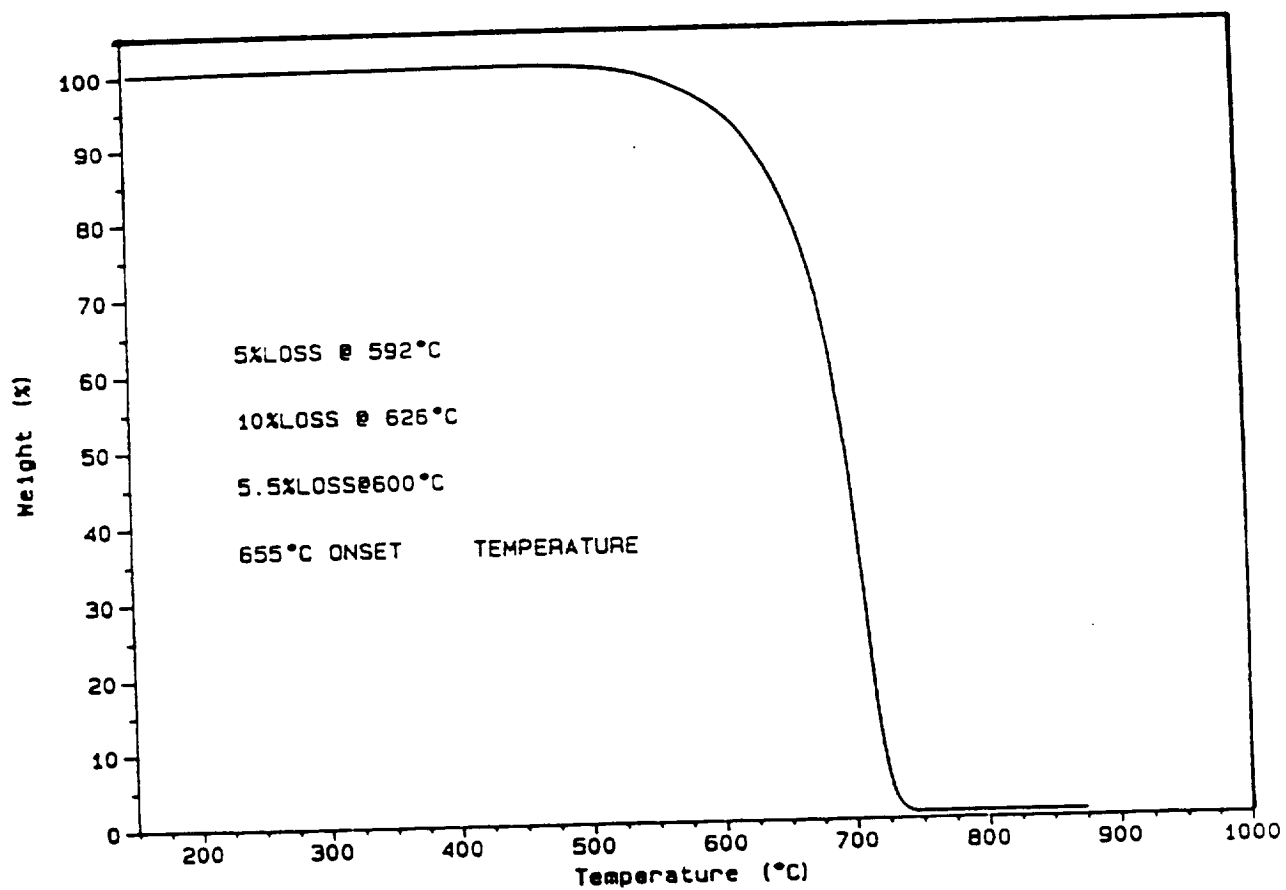
TGA CURVES ON T-40R IN OXYGEN AT HEATING RATES OF 10°C/MIN AND 2°C/MIN.



EXPANSION OF PART OF THE 10°C/MIN TGA CURVE OF T-40R.



TGA on T-40R 12k Carbon Yarn in Air and Oxygen at 10°C/Minute.
"1" in Air; "2" in Oxygen; "3" in Oxygen, Repeat Run.



TGA of T-40R 12k in Oxygen at 2°C/Minute.

OXIDATIVE WEIGHT LOSSES OF CARBON YARNS

em	Yarn	Weight Loss in 1000 Hours in Air			Weight Loss in 1000 Min. in Oxygen 430°C	TGA to 850°C in Oxygen				TGA to 850°C in Air			
		316°C	375°C	430°C		Temp. of 5% Weight Loss	Temp. of 10% Weight Loss	Weight Loss to 600°C	Onset Temp.	Temp. of 5% Weight Loss	Temp. of 10% Weight Loss	Weight Loss to 600°C	Onset Temp.
1	T-300 (1983)	44.5%	-----	-----	64.54	602°C	620°C	4.8%	597°C	668°C	691°C	1.0%	715°C
2	T-300 (1986)	-----	-----	-----	16.73	632	653	1.4	673	700	729	0.4	758
3	T-300 (1985)	-----	-----	-----	26.60	616	637	2.6	647	681	711	0.8	729
4	T-500R (1984)	7.33	-----	-----	24.61	620	638	2.8	641	---	---	---	---
5	Cellion 3000	5.13	88.2	-----	24.97	612	636	2.8	626	---	---	---	---
6	T-300R 3k (1985)	2.98	82.1	-----	14.67	630	655	2.8	676	692	727	1.6	760
7	T-500R 6k (1985)	2.53	83.8	-----	12.26	634	655	2.2	680	697	733	1.0	762
8	T-300R 12k (1985)	2.77	87.2	-----	20.40	633	656	2.2	671	695	732	0.8	750
9	T-40X (20) (1985)	1.27	73.3	-----	10.41	649	670	1.0	702	---	---	---	---
0	T-40R 3k (1985)	0.13	2.32	11.14	0.50	671	708	1.0	741	698	730	0.4	742
1	T-40R 12k (1985)	0.16	2.74	10.63	1.31	669	690	1.0	652	687	714	0.4	742
2	T-40R X-630	0.23	5.35	92.01	0.56	698	735	1.0	775	---	---	---	---
3	Hitco Hltex 46	3.14	40.6	-----	10.09	590	625	5.9	614	---	---	---	---
4	P-55X (1985)	-----	0.40	6.72	0.73	694	724	1.0	654	---	---	---	---
5	P-75S (1985)	-----	1.50	11.90	1.37	710	738	0.4	704	---	---	---	---
6	T-40R 12k (1986)	-----	-----	-----	0.29	704	735	0.3	718	738	768	0	781

ACTIVATION ENERGIES FOR THE CARBON-OXYGEN REACTION*

FOR CHARCOAL, 175-315°C	120 KJ/MOLE	(28.6 KCAL/MOLE)
FOR COKE, 315-538°C	220 "	(52.5 ")
FOR CEYLON GRAPHITE, 482-593°C	370 "	(88.5 ")

*FROM W. K. LEWIS, E. R. GILLILAND, AND R. R. PAXTON,
IND. ENG. CHEM. 44, 1034 (1952).

REFERENCES

1. ASTM Standard Test Method for the Thermal Oxidative Resistance of Carbon Fibers, Method D4102-82.
2. J. B. Barr and B. H. Eckstein, "The Oxidation of Carbon Fibers in Air," Proceedings of the XVIIIth Biennial Conference on Carbon, Worcester, Massachusetts, July 19-24, 1987, p. 9. A fuller version is in process of publication.

The largest uncertainty in the AOT method is in determining the exact length of time that a fiber is exposed to oxidation conditions sufficiently severe to cause weight loss. Our oven takes approximately 40 minutes to reach 430°C with a loaded rack of fibers. After the 16-hour hold, the oven cools to 150°C in approximately 80 minutes. During the heating and cooling periods, the yarn can be expected to undergo an oxidative weight loss that varies with the reactivity of the fiber. Since these weight changes are not separated from the much larger weight loss occurring during the 16-hour hold, it is important that identical heat treatment schedules be used each time.

To establish the magnitude of the weight losses during the heat-up and cool-down periods, a trial was made in which three different carbon yarns were brought to the test temperature and then cooled down again following the regular schedule. The weight losses incurred during this procedure were 0.16% for T-300, 0.73% for T-650/35, and not detectable for T-40R.

Finally, we ran several tests to check on the uniformity of the weight losses measured in the oven as far as the position in the oven is concerned. The results of two such tests are shown in Slides 13 and 14. Alternate hooks were occupied by yarn from one spool of either the new T-650/35 fiber or T-40R. It is clear that there is a consistent difference, small but consistent, between the upper and lower racks which can perhaps be remedied, but the difference is probably smaller than between spools of the same lot or even samples from the same spool.

In summary, we think we have developed an overnight test for the oxidative weight loss of carbon yarns which meets the criteria for a QC or acceptance test and the results of which are useful for predicting the long term stability of the carbon yarns at other test temperatures. The test is easy to carry out and the equipment is not excessively expensive.

C.V. = 11%. The investigation of the reproducibility of the measurements is complicated by a relative lack of knowledge about the uniformity of the materials being studied. The results of replication studies on T-40R, T-300R, T-300 and T-500 are shown in Slides 9 through 12. Additional information to lay a sounder statistical foundation for weight loss limits for various grades is still being obtained.

The proposed AOT involves a few uncertainties which will be of little importance as long as the test is always carried out the same way. One concern is that the fiber finish be completely removed prior to oxidation testing. Most carbon yarns have a size or finish (the terms are used interchangeably) which is applied by the manufacturer to protect the fiber and to improve handleability. The amount of finish is often approximately one weight percent; however, the amount can vary with yarn type and grade. Most standard finishes can be removed by the recommended preliminary heat treatment without damaging the fiber. The oxidative removal of finish is recommended over solvent extraction methods which are tedious, damaging to the yarn, and rarely complete. The burnoff approach may need to be modified for yarns sized with very oxidation resistant high temperature polymers.

Another concern is weight changes which accompany the adsorption of gases from the atmosphere. Carbon yarn, after thermal degassing during finish removal, typically adsorbs about 0.1-0.2% by weight of gases from the atmosphere. As the yarn is oxidized and the surface area is increased, the amount absorbed rises substantially. These sorbed gases introduce an error into the initial and final weights. When yarns are kept in an air-conditioned room at moderate humidity, the error is small and consistent. In a high humidity environment, the error is considerably larger and cooling the fiber in a desiccator is desirable.

Stainless steel screening attached to the racks and a solid stainless steel panel on the upstream side protects the fibers from the high velocity gas flow which damages unprotected yarn. A third rack could be nested in the furnace to increase the number of test samples.

D. A top-loading electronic balance is convenient for rapidly weighing the hanks of fiber. A balance with an accuracy of 0.1 mg is recommended.

The weight losses for PAN-based carbon fiber oxidized by using accelerated test conditions (16 hours in oxygen at 430°C) are listed in Viewgraph 10 along with data from exposures of 1000 hours at 316° and 375°C in air. Fibers with nominal moduli of 42 Mpsi (290 GPa) are the more oxidation resistant yarns and they are sorted according to long term weight loss at the more severe test temperature of 375°C. Since the nominal 32-35 Mpsi (220-240 GPa) fibers often do not survive long term exposure in air at 375°C, data for these fibers are arranged by type according to their behavior at 316°C.

The relationship between AOT weight loss and weight loss at 316°C for fibers in Viewgraph 10 are shown graphically in Slides 6 and 7. Weight losses measured by the two methods are strongly correlated with linear correlation coefficients (r) of 0.969 and 0.879. Weight losses for the 42 Mpsi fiber tested under AOT conditions and oxidation in air at 375°C are plotted in Slide 8. The coefficient of linear correlation for these data is 0.924.

The values for the 16-hour weight losses shown in Viewgraph 10 are averages of four or six different measurements carried out on pairs of samples in two or three different runs. The coefficients of variation ranged from 1.7 to 33%, the higher values being most commonly found for very low weight loss situations. For example, Item 1, T-40R Q60626, gave the following 16-hour weight loss values: 0.54, 0.57, 0.35 and 0.51%, average = $0.49 \pm 0.10\%$ (standard deviation), C.V. = 20%. Similarly, the Celion G-40 IMA-5 (Item 6) gave individual values of 1.96, 1.94, 1.55, and 1.74%, average = $1.80 \pm 0.19\%$,

Two modifications were made to the oven. A Type J calibrated thermocouple was inserted directly into the test chamber and temperatures are monitored on a Marlin Thermicator 412A Digital Indicator. Secondly, to reduce the risk of damage to the heaters or controls by carbon fiber fly, stainless steel screening was inserted over the circulation holes in the walls of the Blue M oven. Slide 5 shows a test rack sitting in the oven, with screens over the circulation ports; the extra thermocouple at the back is plainly visible.

The handling of oxygen and the heating of carbon fibers in an oxygen atmosphere requires strict attention to safety aspects. We have performed the AOT in the Blue M oven repeatedly without incident. After the initial purge, the flow rate of oxygen in the oven is set at 2 l/min ($4.2 \text{ ft}^3/\text{hr}$) which is more than adequate to ensure an ample supply of oxygen for the oxidation reaction. The oven has a chamber volume of 165 l (5.8 ft^3) and a full load of 72 three-gram samples of carbon yarn (18 moles of carbon) would require 450 l of oxygen (room temperature and pressure) for complete combustion. In practice, weight losses average 20% for the more reactive T-300 type carbon fibers and only 1% for the most oxidation resistant yarn (T-40R).

C. The sample rack for holding the yarn samples during testing is actually a pair of stainless steel racks, with the smaller one fitting inside the larger one. Two pairs of these rack assemblies were constructed so that one pair could be loaded while the other is in use. To fit the Model IGF-7780-4 oven, the larger of the two racks is 16 inch high x 18 inch deep x 22 inch wide and the smaller rack is 9 inch high x 17 inch deep x 21 1/2 inch wide. Each rack consists of a frame of 1/2 inch strips with four rods across the top to which are welded nine hooks on 2 1/4 inch centers. Each hook has a 1/4 inch radius of curvature. There are a total of 72 hooks spaced so that the suspended yarns do not touch.

programmed to turn off the heating elements in early morning and allow the yarn to cool in the oxygen atmosphere. The test rack is removed from the oven and, when the yarn has cooled to room temperature, the fibers are weighed. The weight loss may then be calculated or a suitably equipped balance can do the calculation automatically.

The apparatus required for the AOT consists of four parts: A device for winding the sample hanks (home-made), a test oven, two racks on which to expose the samples in the test oven (also home-made), and an analytical top-loading electronic balance.

A. The sample winder is shown in Slide 2. It consists of a 1/50 hp Bodine DC motor and speed control driving a brass wheel on which four Teflon-covered brass screws are mounted. These are shown in Slide 3. Two opposing screws are fixed, while the other two are spring-loaded. The hank of sample yarn is wound on these four Teflon posts. A footage counter and knowledge of the yield of each yarn in m/g is helpful in collecting the three-gram samples. The holder for the yarn supply spool is on a separate stand.

To insure that the test fibers have not been handled with bare hands or contaminated from other sources, the outer layers of fiber are stripped from the package and test samples taken from an inner portion. Fibers are handled with clean gloves and stainless steel tweezers.

B. The test oven selected for the AOT is a Blue M Inert Gas Oven, Model IGF-7780-4, shown in Slide 4. The chamber size was more than adequate for our purposes. As installed, the oven can run with air, oxygen, or nitrogen atmospheres. A duct carries the exhaust gases outside the building which avoids a possibly hazardous buildup of oxygen in the laboratory. Blue M makes this type of oven in four sizes, shown in Viewgraph 9, and we considered the next-to-smallest adequate.

While investigating the effect of extended times on a standard test, the effect of a longer exposure to oxygen at 430°C was also examined. A series of samples was run for 48 hours in the TGA apparatus and the results obtained are also shown. No differences in ranking and no startling behavior were observed. A typical curve is shown in Viewgraph 8. Note that the weight loss curve is not linear and, hence, once again extrapolation becomes difficult.

Another aerospace company has an oxidation specification which is basically an acceptance test. The test samples are first heated in a vacuum oven at 176°F (80°C) for 16 hours to remove finishes, but that will not happen. Then samples are heated in air at 710°F (377°C) for 24 hours. The results obtained by this method also do not correlate well with long term exposures at low temperatures. There are several other, similar, tests in use, none really useful except perhaps as acceptance tests.

Now let us consider the proposed accelerated oxidation test (AOT), which consists of four steps. First, finish and volatiles are removed from the yarn by a preliminary heat treatment in air. The thermally cleaned fibers are weighed and the oxidation resistance is tested by heating the fibers in flowing oxygen at $430^{\circ}\text{C} \pm 3^{\circ}\text{C}$ for 16 hours. Finally, the fibers are cooled to room temperature and reweighed to permit calculation of the weight loss. The test is outlined in Slide 1.

Duplicate samples of each yarn to be tested are wound into hanks weighing about three grams and placed on a test rack. Finish is removed by heating the fibers on the test rack in air to at least 260°C. In the tests described here, the finish was removed by heating to an oven temperature of 300°C in air, then allowing the yarn to cool slowly. Next, each hank is weighed on an electronic top-loading balance capable of ± 0.1 mg accuracy. The loaded test rack is reinserted into the oven, an oxygen valve is opened, and the yarn is oxidized at 430°C in flowing oxygen for 16 hours (overnight). The oven is

The same type of behavior was shown by almost all of the oxidation resistant yarns (the new T-40R and the pitch-based yarns) and may, therefore, be considered typical for this type of material. This shows that reasonably rapid TGA in oxygen is not a useful characterization technique, at least if carried beyond about 650°C. But the most serious drawback to isothermal TGA is that the expensive apparatus can run only one or perhaps two samples per night, the samples are small (< 30 mg), and the precision of the measurements is not satisfactory.

Now consider some weight-loss-at-constant-temperature tests. In the ASTM Method D4102-82 mentioned before, the finish on the yarn is first removed by solvent extraction. We do not consider this a prudent procedure because not all finishes are soluble, especially not in the MEK the procedure calls for, the finish may not be removed completely, and the yarn is usually damaged in handling. The actual weight loss due to oxidation is measured for 24 hours in 375°C, a condition under which very few modern fibers show any measurable weight loss.

One aerospace company has a specification applicable to carbon fabrics for space shuttle applications. The procedure calls for measuring the weight loss of a fabric in a TGA apparatus in flowing air for one-half hour. The initial heating rate is to be very rapid. The data obtained are shown in Viewgraph 7.

The viewgraph shows the test results obtained in air at 525°C. Even though the test only calls for a one-half hour exposure, a two-hour exposure was considered more meaningful for the oxidation resistant materials in which we are principally interested. The correlation between the 525°C weight losses and long term weight losses at 316°C and 375°C are much poorer than the correlations in the proposed AOT test.

much on the shape of the curve, and the result is not always meaningful. For example, in most instances, the "onset temperature" as defined in this program is higher than the temperature at which 5% of the weight has been lost, which is patently ridiculous; the situation is shown in Viewgraph 3. Now back to Viewgraph 2.

The temperature of the 5% (or perhaps 10%) weight loss is more meaningful. There is a fair correlation of these temperatures with the long term weight loss in air, but their total range is only about 110°. The method may be fine for the very oxidation resistant yarns, but examination of the data for Items 1, 4, and 5 suggests that for relatively high weight loss yarns, the method lacks accuracy. The best correlation with long term weight losses was shown by the overnight weight loss in oxygen at 430°C.

One other interesting phenomenon was observed with some TGA's in oxygen, behavior which precludes the use of TGA as a QC tool for very oxidation resistant yarn except at time-consuming very low heating rates. Examine Viewgraph 4. All three curves are on the same yarn, T-40R 12k. Curve 1 was taken in air. Curve 2 was taken in oxygen, and because it seemed so strange, the run was repeated. The repetition is shown as Curve 3, and the same type of behavior was seen again. Viewgraph 5 shows the same data as Curve 2, but now the weight and temperature are plotted against time (the heating rate was 10°C/minute). Normally, the temperature versus time curve is a straight line. The blip seen suggests a sudden, strongly exothermic reaction. The region of the blip is shown on an expanded scale in Viewgraph 5. We suspect that the oxidation resistant yarns have a much later onset of oxidation, but once the exothermic oxidation begins, the sample may get so hot that the carbon actually begins to burn, leading to the observed rapid rise of some 60° in the temperature of the sample, rapid weight loss, and enough turbulence accompanying the combustion that the weight readings become meaningless. The problem can be avoided by running the TGA very slowly, so that the sample oxidizes in a smoother fashion and does not actually catch fire. Such a TGA of the same yarn at 2°C/minute is shown in Viewgraph 6.

the time some specified temperature is reached, or the temperature at which a particular percent weight loss is reached. In addition, programs exist which allow the calculation of activation energies and from these the time in which a material would lose a specified fraction of its starting weight at a given temperature. This last is the procedure used by C. H. Sheppard of Boeing, but it is a method about which we have serious misgivings because the extrapolation used is linear while the actual behavior of the carbon yarns is not.

In the initial efforts to find a QC method, thermogravimetry (TGA) was investigated and, in fact, the AOT was first developed using a DuPont 990 Thermal Analyzer for isothermal weight loss studies as well as in its more conventional (changing temperature) modes. Some results from the study are shown in Viewgraph 2 which also contains the results of some long term oxidation studies with which the QC method must correlate. Then there are the TGA weight losses on all of the yarns in oxygen in 1000 minutes at 430°C. One thousand minutes are 16.67 hours, which is an overnight run on an unattended instrument. Runs at 316° and 375°C were not useful.

Another thermogravimetric method was the TGA-to-850°C weight loss curve in oxygen. Information extracted included the temperatures at which 5% or 10% of the initial weight was lost, the weight loss to 600°C, and the temperature of the onset of oxidation. Let us dispose of the last two items first. The weight loss to 600°C is too small to be useful as a QC tool and is in no way related to the long term weight loss. Probably different mechanisms operate when the temperature rises above 450°C. The onset of oxidation is difficult to define. Ideally, it should be the temperature at which a discernible weight loss first occurs, but that is hard to determine. The way the instrument software defines the onset of oxidation is to draw extrapolated straight lines from the early portion (nearly horizontal) of the weight loss curve and from the steep (vertical) portion. The point at which they intersect is called the onset of oxidation, but those two slopes depend very

fibers will not show significant weight losses. Short term tests (less than 100 hours) at the use temperatures of polymeric composites (300°-400°C) in air are better suited to check lot-to-lot consistency of the same grade. The mechanism of carbon fiber oxidation involves the formation of surface complexes of carbon and oxygen, many of which are relatively stable. Carbon samples often show a weight gain during the first few hours or days of oxidation. Therefore, the initial stages of a weight loss curve cannot be correlated with the long term weight loss. Furthermore, the shape of the initial weight loss curves depends on fiber type and oxidation temperature. Obtaining a substantial weight loss in a short time requires the use of temperatures well above the intended use temperature, but the mechanism of oxidation and, therefore, the activation energy depends in part on the temperature (Viewgraph 1). Hence, extrapolation of weight loss data over any significant temperature interval is not accurate or useful.

In a paper which we gave at last year's Carbon Conference,⁽²⁾ we showed that the mechanism of carbon oxidation probably does not change significantly from 300° to 430°C, though it does begin to change above that temperature. Hence, 430°C was taken as the maximum acceptable test temperature. Also, the oxidation rate is increased substantially, as expected, if air is replaced by oxygen. Hence, a new method was developed using oxygen at 430°C as the test environment. But before discussing the new method, which we call the AOT for accelerated oxidation test, I want to mention some of the methods proposed by various other organizations.

Thermogravimetric measurements have become widely used for both research and QC purposes, in part because reliable and simple instruments are commercially available along with various software packages which allow the rapid calculation of many different characteristics. Most thermogravimetry involves weight gains or losses as a function of temperature at specified heating rates. QC parameters allegedly readily calculated by available software include the temperature of the onset of oxidation, the weight loss by

AN ACCELERATED OXIDATION TEST FOR OXIDATION RESISTANT CARBON FIBERS

A Talk Given by Bernard H. Eckstein at GE-Evendale in August, 1988

This talk is a preview and an expanded version of a paper which will be presented by Jack Barr at the SAMPE Conference in Minneapolis next month. The work described was started almost two years ago. Amoco needed a reasonably rapid quality control test for its oxidation resistant carbon fibers and considerable work had convinced us that the existing short time tests did not correlate well with long term oxidative stability. At the same time, GE wanted to develop an acceptance test and it made sense to try to have the two tests identical. Amoco was willing to share its findings with GE and the industry, thus eliminating a lot of duplication of efforts. I have twice before discussed the work here at Evendale as it progressed.

I need to offer an apology for the somewhat disorganized talk; Jack Barr had slides made for the SAMPE presentation, but my talk will be longer and is being fleshed out with viewgraphs, so the two are being intermingled. I only found out that I was to give this presentation when I returned from vacation last week.

As indicated above, the development of special oxidation resistant grades of carbon fibers for use in high temperature polymer matrix composites has created a need for a reasonably rapid fiber oxidation test suitable both as a quality control test for the manufacturers and as an acceptance or evaluation test by the customer. So far, the only reliable data have been obtained by long term heat aging at temperatures close to the intended use temperatures, for example, measuring the weight loss of samples in air at 600° or 700°F in 1000 hours. Such tests are clearly not suitable for the purposes stated above. ASTM Method D4102-82⁽¹⁾ calls for the exposure of carbon fibers for 24 hours in air at 375°C; under those conditions, good oxidation resistant

APPENDIX J

BERNARD ECKSTEIN'S PRESENTATION
(WITH MILES TOWNE'S PERMISSION)

FUTURE WORK

- 1. LARGER EFFECTIVE DIAMETER FILTER**
- 2. PURE RESIN**
- 3. USP-28**

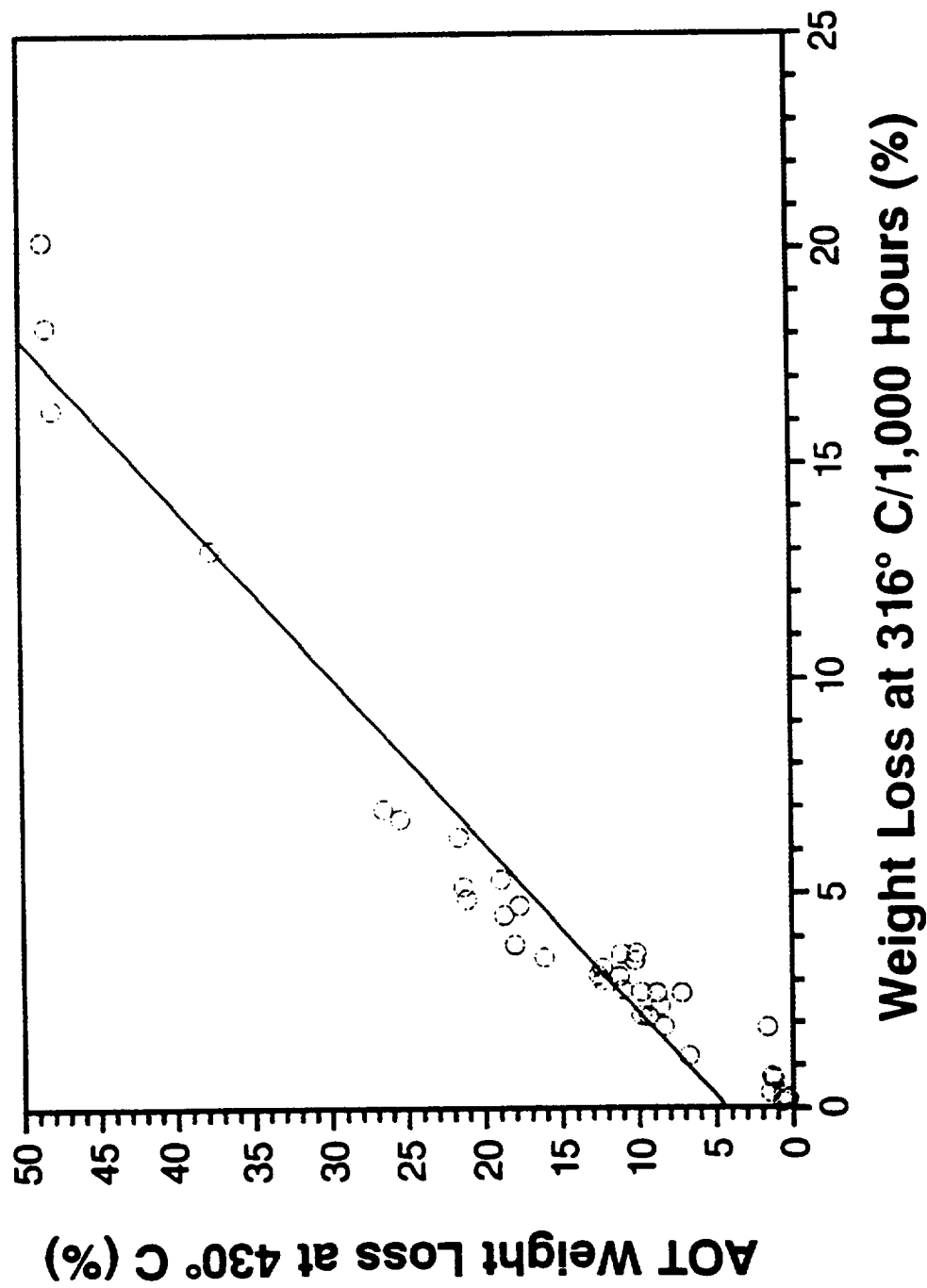
Accelerated and 1000-Hour Weight Losses of PAN-Based Carbon Yarns

Item No.	Yarn Type	Trace or ID No.	% Weight Loss in 16 Hours in Oxygen at 430°C	% Weight Loss in 1000 Hours in Air at 316°C at 375°C	
<u>42 Mpsi Modulus</u>					
1	T-40R	Q60626	0.49	0.20	1.64
2	T-40R	Q51215	0.81	0.13	2.37
3	T-40R	Q70314	0.83	0.27	3.09
4	T-40R	Q70315	1.64	0.35	4.85
5	Celion G-40 IMA-7	J10141-J Lot 5Y62	1.41	0.66	13.5
6	Celion G-40 IMA-5	J0107-J Lot 5962	1.80	1.87	21.6
7	HiTex 42-6A	Lot P195-1	1.52	0.72	27.8
8	Apollo 12k E/IMS	Rel. #5117	6.93	1.27	45.5
9	T-650/42	12F1113E	8.55	1.89	89.0
10	T-650/42	6G0111	9.50	2.12	91.4
11	T-650/42	12F0821	11.4	3.08*	----
<u>33 Mpsi Modulus</u>					
12	T-300R	3E0820J	9.86	2.16	----
13	T-300R	12F0607	8.77	2.37	93.6
14	T-300R	12E1216	12.5	2.98	82.1
15	T-300R	12E1217	12.5	3.11	88.0
16	T-650/35	6G0429B	11.2	2.77	90.6
17	T-650/35	6G0505B	10.4	3.46	90.5
31	T-500	3F1008	7.38	2.69	80.3
32	T-500	6F0129	9.88	2.71*	----
33	T-500X	12D1198	21.5	5.16	92.9
18	T-300	6G1018	8.99	2.69	----
19	T-300	3F0527	12.5	3.29	----
20	T-300	3F0516	16.3	3.54	----
21	T-300	3F0407	11.3	3.62*	98.0
22	T-300	6E0409	10.3	3.63*	----
23	T-300	3F0301	18.2	3.84	----
24	T-300	3F1008B	18.9	4.51	----
25	T-300	3F0909	17.9	4.72	----
26	T-300	3F0203	21.3	4.87	----
27	T-300	3F1019B	19.1	5.32	----
28	T-300	3F1102	21.8	6.30	----
29	T-300	12E0601	25.6	6.72	----
30	T-300	3F1130	26.7	6.95	----
34	Celion G30-500	HTA-7E	37.8	13.0	----
35	Magnamite AS-4	X-432-5A	48.0	16.3	----
36	Celion G30-600	STA-7C	48.4	18.4	----
37	Celion G30-500	HTA-7C	48.6	20.2	----

* Extrapolated from data to 800 hours in an interrupted test.

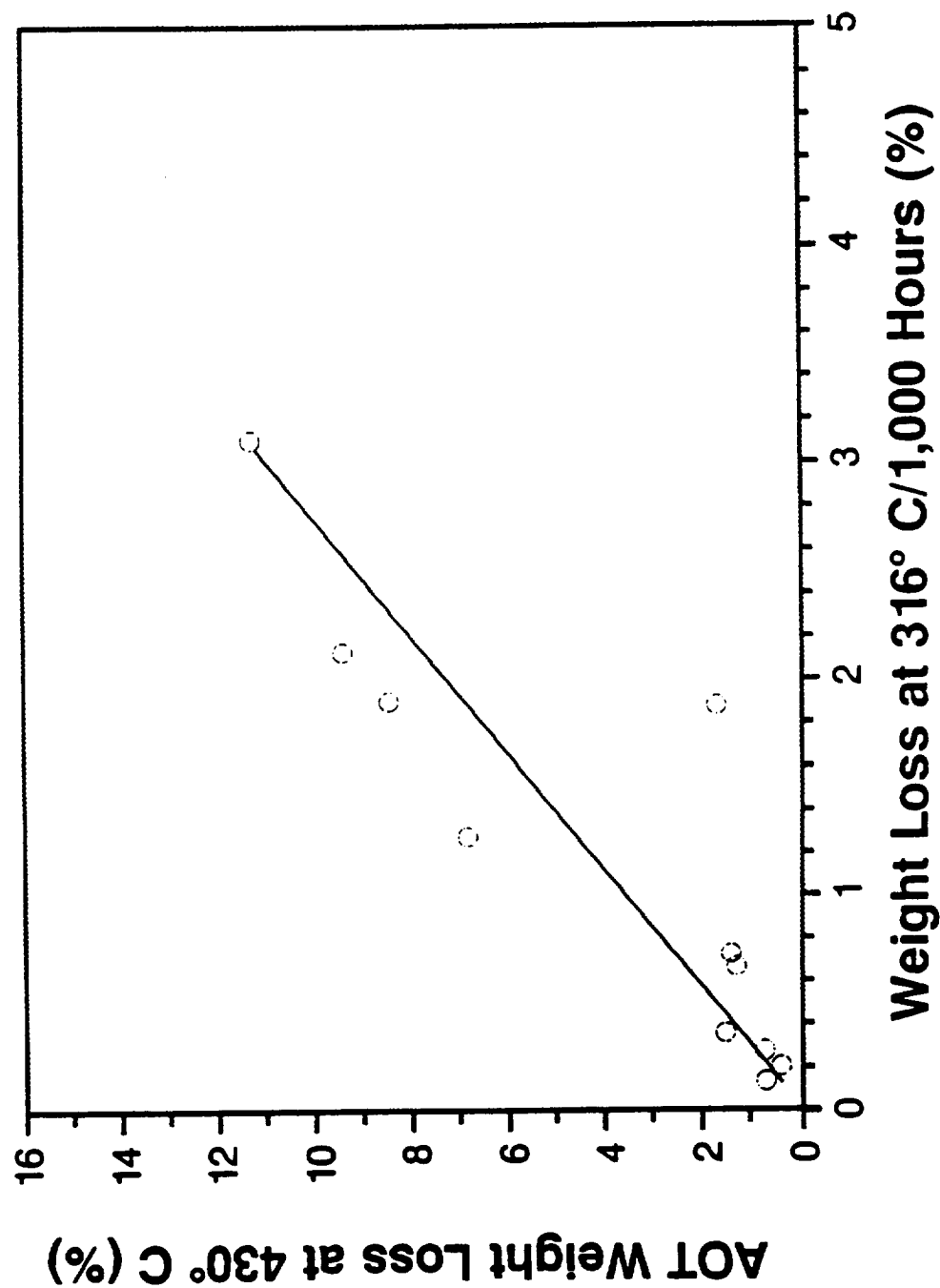
AOT VS. 316° C/1,000 HOURS

33 MSI and 42 MSI Modulus Fibers



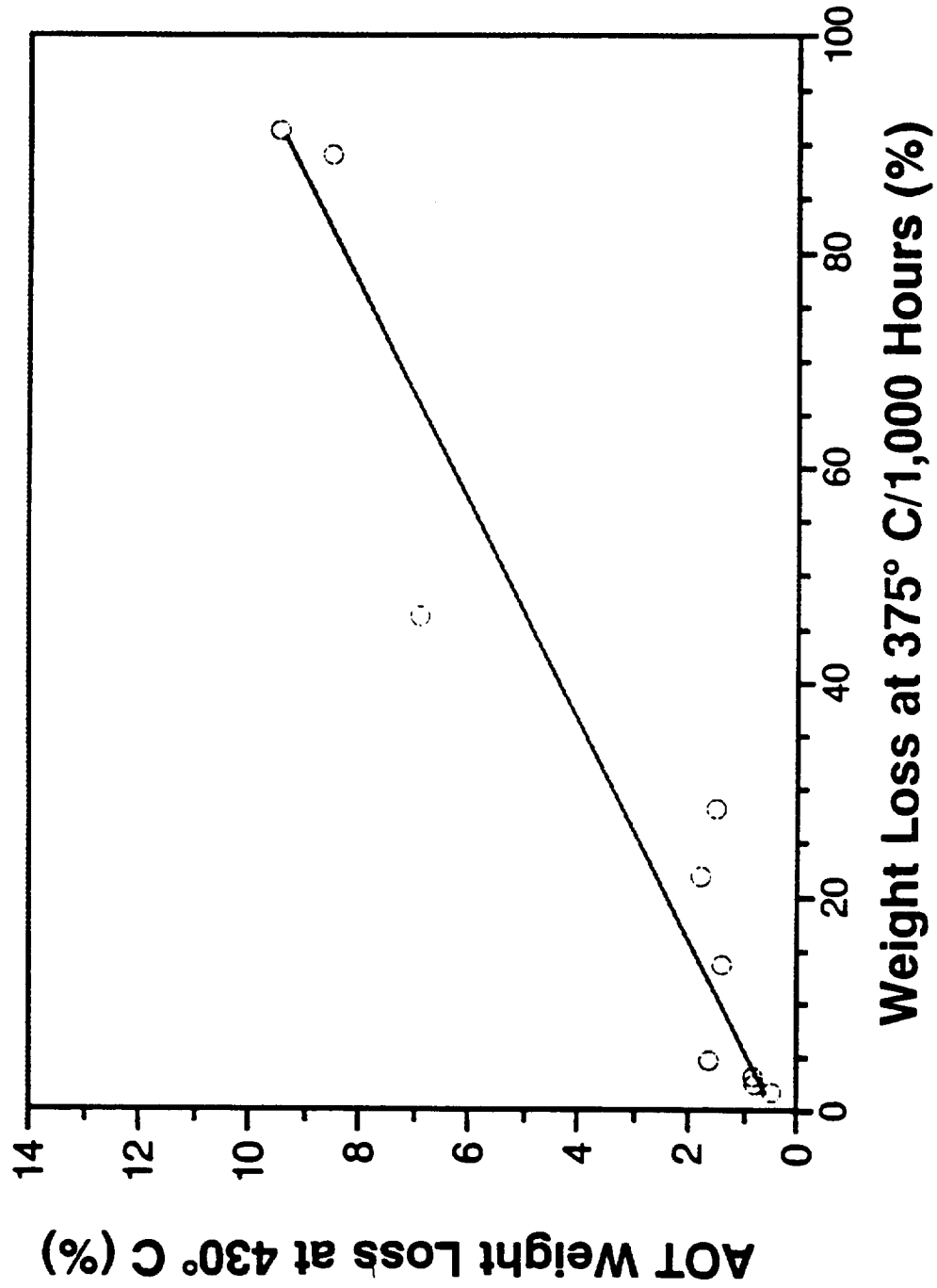
AOT VS. 316° C/1,000 HOURS

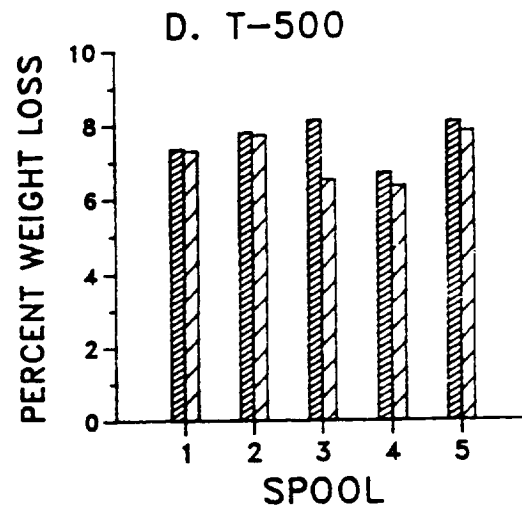
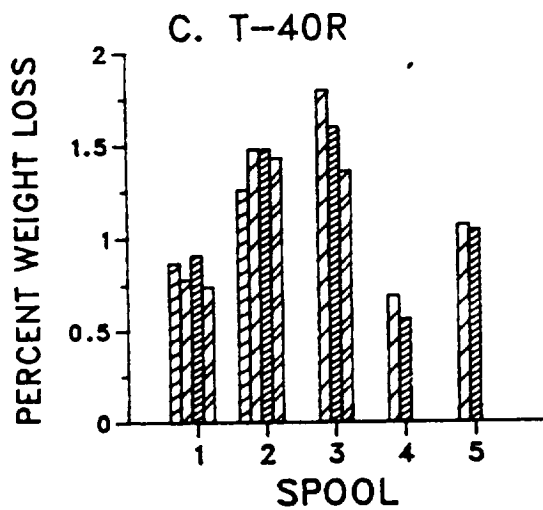
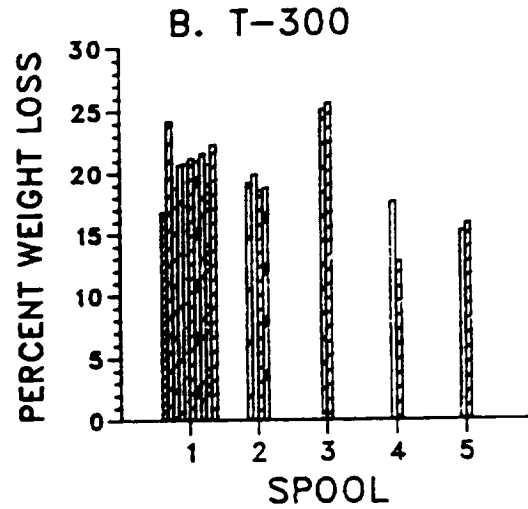
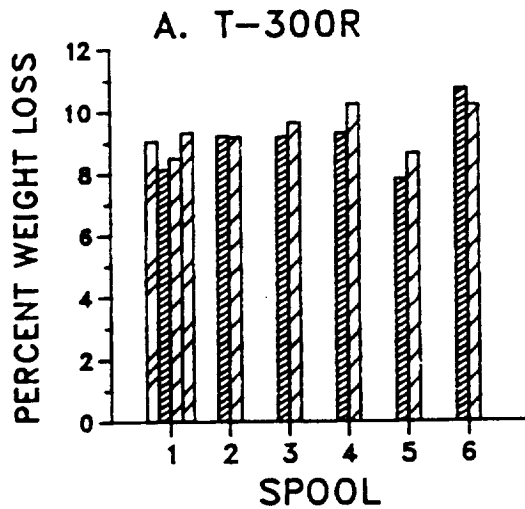
42 MSI Modulus Fibers



AOT VS. 375° C/1,000 HOURS

42 MSI Modulus Fibers

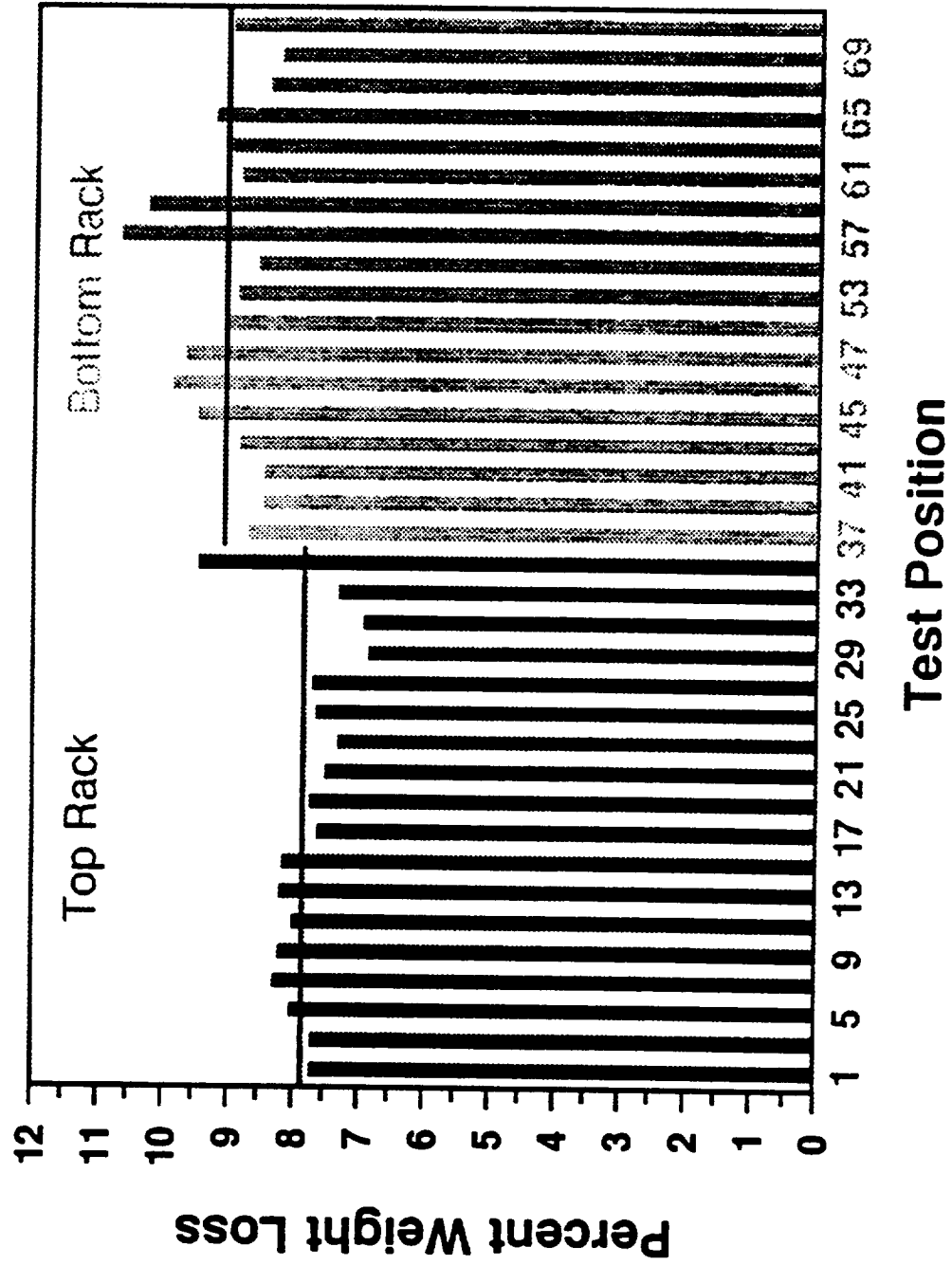




Replicability Studies on Various Carbon Yarns Taken from Different Spools of the Same Lot. C.V. = 8.9% for T-300R, 10.0% for T-300, 33% for T-40R, and 8.8% for T-500.

REPEATABILITY WITHIN TEST OVEN

T-650/35 Fiber



REPEATABILITY WITHIN TEST OVEN

T-40R Fiber

